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(Unclassified Title)

HIGH ENERGY OXIDIZER STABILIZATION

A. D. McElroy
J. W. Nebgen
Midwest Research Institute

Contract No. AF 04(611)-11199
December 1966

1967

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FOREWORD

This program has been conducted at Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri, 64110, under the general supervision of Mr. R. L. Hughes, Head, Physical and Inorganic Section. Mr. A. D. McElroy, Principal Chemist, is project leader. Personnel contributing to the program are J. W. Nebgen, W. V. Best, F. E. Welsh, and G. C. Chaplin. The program was monitored by Mr. James L. Trout and 1/Lt. Ray Foscanti, RPCS, Edwards Air Force Base.

The research covered by this report has been conducted under Contract No. AF 04(611)-11199, AFSC Project No. 3148 (Midwest Research Institute Project No. 2909-C) and covers the period 15 September 1965 - 14 September 1966.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

This technical report has been reviewed and is approved.

W. H. EBELKE, Colonel, USAF
Chief, Propellant Division

ABSTRACT

The compatibility of nitronium perchlorate with various organic materials, including a solid propellant binder system, has been investigated. Infrared and electron paramagnetic resonance spectroscopy were employed to measure reactivity.

The results indicate compatibility between raw NP and the binder system to be less than satisfactory. Studies of simple hydrocarbons gave the following results. Hexane, n-pentane and isooctane react slowly with NP, at ambient temperatures; HNO_3, NO_2Cl, N_2O and CO_2 are major reaction products. Methane does not appear to react. Ethane, propane and neopentane are not detectively consumed by NP, but nitric acid is generated in small quantities along with perchloric acid. It has been tentatively concluded that the latter substances react very slowly with NP.

Chlorine dioxide is inherently present at low concentrations in dry, commercial NP. Concentrations are slightly higher in undried NP. Addition of NP to water, $HClO_4$, HNO_3, H_3OClO_4, and all tested organic substances except methane resulted in increased ClO_2 concentrations. Two samples of Reta-coated NP contained higher than normal concentrations of ClO_2. One concludes generally that NP is slightly unstable at ambient temperatures, that substances inherent in NP enhance the instability, and that added foreign substances promote ClO_2 formation. The formation of ClO_2 can be used as a qualitative measure of the reactivity of organic materials.

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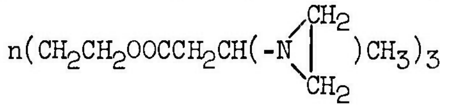
GLOSSARY OF CODE TERMS

NP:	nitronium perchlorate, NO_2ClO_4.
NP fluff:	finely divided powder, as originally manufactured by Callery Chemical Company.
NP granules:	compacted, granular NP, 8-20 mesh; supplied by Thiokol Chemical Company, Elkton Division.
Reta-coated NP:	granular NP coated with a polymer; Union Carbide.
UTREZ:	carboxy terminated polyisobutylene, acid equivalent weight of about 1100. Enjay Chemical Company.
NTEB:	nitrotriethyl-β-ethyleniminobutyrate; American Cyanamid Chemical Company;  $n(CH_2CH_2OOCCH_2CH(-N\begin{matrix}CH_2\\ \vert\\ CH_2\end{matrix})CH_3)_3$.
MRPX:	an isoparaffinic hydrocarbon oil; Shell Oil Company.
Soltrol-200:	a paraffinic mineral oil; Phillips Petroleum Company.
CHP:	cyclohexylpiperidine.
HMT:	hexamethylenetetramine.
EPR:	electron paramagnetic resonance spectroscopy.
FMIR:	multiple internal reflectance infrared spectroscopy.

I. INTRODUCTION

Nitronium perchlorate (NP) is an oxidizing compound with several noteworthy properties: (1) a high performance potential in solid propellantry; (2) high reactivity, and (3) inherent stability nominally suitable for propellantry, but which imposes irritating restrictions on the propellant processor. No little effort has been devoted to efforts to tame the compound, to develop solid propellants in which NP is the oxidizer. These efforts have not to date been successful, though remarkable strides have been made, and at times it has appeared that various problems were close to solution.

This program was initiated for the express purpose of developing and applying techniques capable of measuring compatibility and propellant stability at the laboratory level, so that evidence of compatibility or the lack thereof could be obtained in reasonably short times. A further requirement of a technique is data indicative of the nature of instability, so that causes and effects can be deduced, and remedial measures will hopefully become obvious.

Infrared and electron paramagnetic resonance spectroscopies were selected for use in this study. EPR has the advantage in theory of being able to detect small in situ changes in NP-containing systems. NP is potentially a rich source of the NO_x and ClO_x family of radical molecules, and in addition radicals typical of oxidizer-fuel reaction are a possibility. Infrared methods are substantially less sensitive to the small change than is EPR, but are more likely to give data which can be used to define reactions. Internal reflectance infrared has been used extensively to observe condensed phases containing NP, and the more usual gas cells have been employed to observe species evolved into the gas phase.

The objective of the program as originally conceived was essentially to obtain a more definitive picture of the compatibility between NP and binder constituents than is possible through the normally employed observations of gassing and changes in physical and combustion properties. We specifically were interested in the detection, monitoring and characterization of reaction as it occurred at oxidizer-fuel interfaces.

The binder system selected for study is that developed by the United Technology Center (Ref. 1). At the time of the inception of the program the UTC efforts had succeeded in achieving near compatibility with a high performance binder. The shelf-life of cured propellants containing uncoated NP was less than satisfactory, however, and it was beginning to be apparent that protective coatings (e.g. the Reta coatings developed by Union Carbide (Ref. 2) or surface passivation - possibly both - might be required. Early results indicated the state of compatibility to be less than that deduced from observations of bulk propellant properties, and we therefore directed some effort toward a general characterization of the reactivity of NP with carbonaceous materials. In the latter effort we were concerned with two questions: (1) Is NP inherently compatible with the C-H and the C-C bond? and (2) What are the structural and practical boundaries of compatibility?

Another area of interest involved certain fundamental properties of NP which apply to its use as an oxidizer in solid propellant systems. The EPR studies yielded information relevant to both the stability of NP and to its reactivity. Infrared studies served to emphasize the significance of certain known properties of NP.

It is appropriate at this point in the report to state that the results of the program give little cause for optimism about the future of NP as an oxidizer in solid propellants. The reader is so forewarned so that he may be appropriately critical of the data and derived conclusions.

II. DISCUSSION

A. The Reactivity of NP

NP is the anhydride of nitric acid and perchloric acid, and thus is strongly acidic in its own right. Most of its reactions can be explained by this property. NP thus generally reacts readily, even violently, with Lewis bases. Among the reactive organic functionalities are the olefinic double bond, ROH, $R_2C=O$ and $R_xNH_{(3-x)}$ (Ref. 2). The chloride ion, nitrate ion, and carbonate ion are slowly reactive (Ref. 3), and halogens bonded covalently to amphoteric metals are generally more reactive. It is popular to attribute reactivity to the nitronium ion, since the acidic character of NP resides principally in the cation. This picture is substantially correct, in that initial attack is undoubtedly on the cation. However, the perchlorate ion is often not an innocent bystander, and control of reactions involving the nitronium ion requires a stable perchlorate as a by-product. Organic reactants can be expected to fail on this point. The nitronium ion logically will form organo-nitrates, nitroorganics and nitric acid as initial reactants, and the perchlorate ion has little choice but to form perchloric acid or organo-perchlorates. Neither by-product is stable or unreactive. If amines are present, substituted ammonium perchlorates can form, and these generally will be relatively stable and unreactive. Generally, however, it is obvious that trouble must be anticipated, if reaction is permitted to initiate; reactivities of by-products are not likely to be less than the reactivity of NP, volatile and reactive secondary by-products are to be expected, and water of combustion will contribute to reactivity by hydrolyzing NP.

In comparison, the reactivity of ammonium perchlorate is essentially the reactivity of the perchlorate ion. Furthermore AP is less readily attacked by by-products of reaction, and the effect of water on AP is one of aquation rather than hydrolysis. It follows then that stability in an NP system comparable to stabilities of AP systems demands a greater resistance by NP to initiation of reaction than is the case with AP. This is a very stringent demand or requirement for a material as reactive as nitronium perchlorate.

The very ready hydrolysis of NP is a property of importance from a reactivity standpoint. General experience has shown that "wet" or "undried" NP is more reactive than dried NP, and that dry reagents (propellant ingredients) are more compatible with NP than are undried substances (Ref. 1). Special handling and processing procedures are thus an obvious requirement.

B. The Stability of NP

We have not specifically studied this question, as have others. By way of review, NP decomposes rapidly at temperatures above 100°C (Ref. 4), and relatively slowly at lower temperatures. The rate of decomposition at about 50°C is so slow that meaningful data are difficult to obtain by usual procedures. Induction periods precede the onset of decomposition, and the length of the induction period is a function both of temperature and of purity. Added water (Refs. 5 and 6) is particularly effective for lengthening the induction period, a fact which at first glance appears inconsistent with the effect of water upon reactivity.

Nitrosonium perchlorate and oxygen are major products of the slow decomposition of NP (Ref. 6), and this fact suggests that the mode of decomposition consists of loss of oxygen from the NO_2^+ ion followed by decomposition of $NOClO_4$.

$$NO_2^+ClO_4^- \longrightarrow NO^+ClO_4^- + \tfrac{1}{2}O_2$$

$$NOClO_4 \longrightarrow \text{volatile products}$$

It has been suggested (Ref. 6) that a non-ionic intermediate, $NO_2ClO_4^*$, must be formed before release of oxygen. This intermediate has been suggested also to account for the low volatility of NP.

C. Materials and Procedures

As stated earlier in this report, the binder system employed in the program is that developed at the United Technology Center (Ref. 1). The binder ingredients are UTREZ, a dicarboxylic acid with a polyisobutylene backbone developed by UTC and the Enjay Chemical Company, NTEB (nitrilotriethyl-β-ethyleniminobutyrate), an aziridinyl curing agent (American Cyanamid); and MRPX, a paraffinic mineral oil plasticizer (Shell Development Co.). The NTEB was employed as supplied. NRPX and UTREZ were supplied to us by UTC; both were pretreated at UTC to minimize reactivity with NP by procedures described in reference 1. Soltrol-200, a paraffinic mineral oil (Phillips Petroleum Co.), and Vistanex LMMS (Enjay), a viscous polyisobutyle , were employed in preliminary studies which dealt with development of infrared techniques. The Soltrol-200 mineral oil was pretreated with fuming nitric acid, dried, and vacuum distilled, while Vistanex was used as received.

Other organic substances tested for compatibility with NP are methane ethane, propane, neopentane, n-pentane (Phillips research grade), hexane (Fisher, mixture of isomers), isooctane (Phillips research grade), methyl chloride, and ethyl chloride. Unless otherwise specified above, these were supplied by the Matheson Company in the highest available purities. In nearly all instances the hydrocarbons were treated in some manner to remove water; these treatments will be described later.

1. Multiple internal reflectance infrared spectroscopy: A method capable of looking as directly as possible at the oxidizer-fuel interfaces was desired. For this purpose multiple internal reflectance infrared (Refs. 7 and 8) (FMIR) was selected for investigation. Silver chloride plates, 50 mm x 20 mm x 2 mm, with both ends cut at an angle of 60° to the axis of the plate, and with both sides (20 mm x 50 mm) highly polished, served as the reflectance plates. Incident infrared radiation enters the plates at one end, is multiply reflected internally, and exits from the other end to the detector. Substances properly mounted on one or both of the flat surfaces of the plate attenuate the radiation, and infrared spectra typical of the substances result. For our purposes exclusion of the atmosphere was mandatory. This requirement was met by using the liquid sample holders (Figure 1) supplied by the Wilks Scientific Corporation. Teflon "O" rings hold the silver chloride plate in place, and at the same time provide an air tight seal.

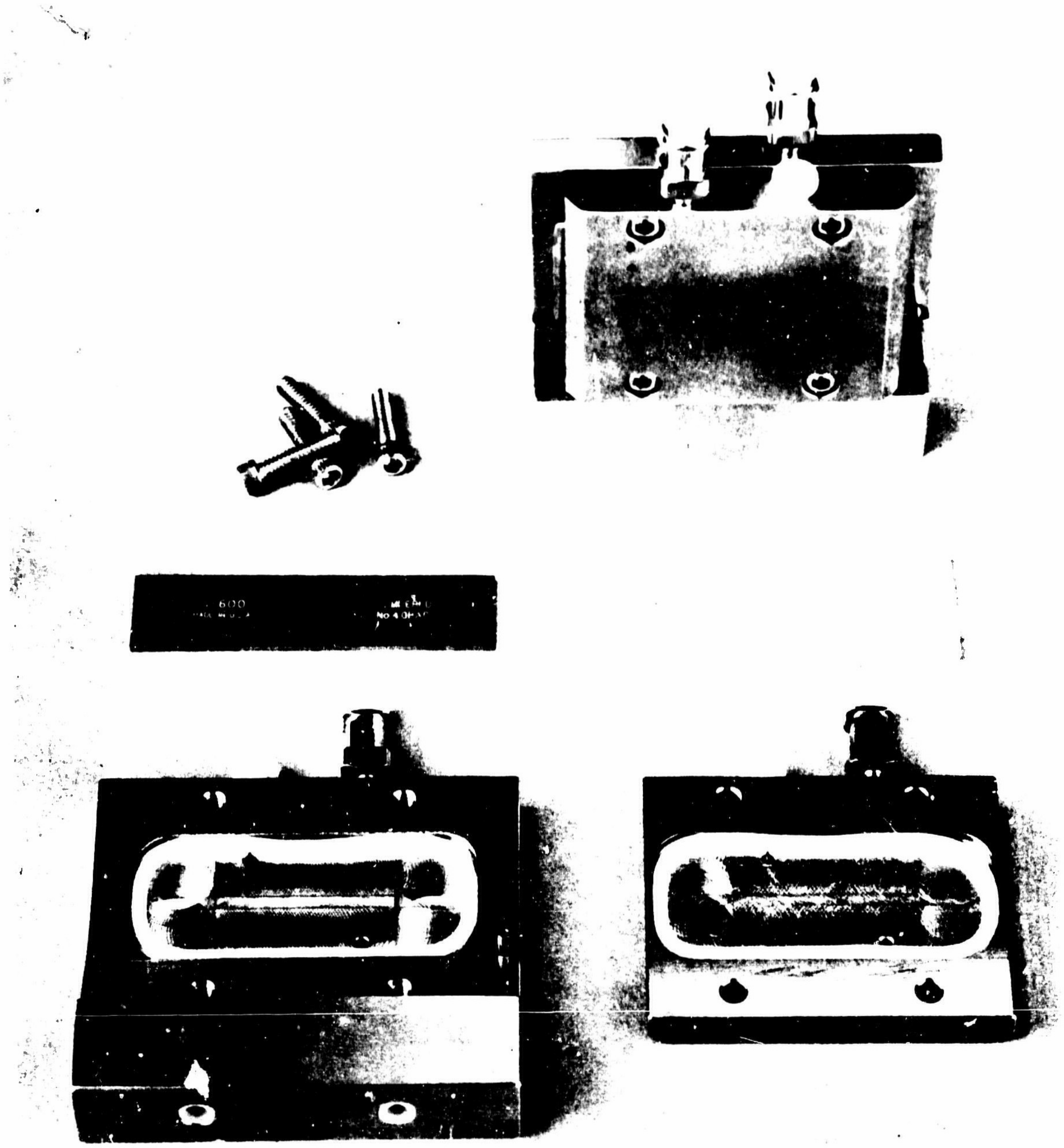


Figure 1 - FMIR Liquid Sample Cell with Silver Chloride Plate

Three techniques were employed to prepare and mount samples for examination by FMIR. One technique consisted of wetting NP fluff with sufficient organic material to prepare a thick paste which was then spread uniformly over the plate. In a second method, a thin film of an organic liquid was spread on the plate, and NP fluff was dusted over the film. The third method consisted of withdrawing a semi-solid slurry of NP from a vial containing NP and liquid organic materials. Liquid phases were simply spread over the plate. All these techniques were satisfactory.

2. Transmission infrared: Standard gas cells equipped with a side arm were employed extensively to identify volatile species arising from NP containing systems. NP was placed in the sidearm along with liquid reactants. Gaseous reactants were admitted at pressures ranging from 20 mm to 50 mm. In some experiments gases were withdrawn periodically from flask reactors and examined by infrared. Spectra were obtained on the Beckman IR-12 instrument.

3. Electron paramagnetic resonance spectroscopy: In initial studies vycor EPR tubes were fabricated from 10/30 standard taper inner joints. A majority of the EPR data were obtained with Varian 3 mm ID EPR tubes, which were sealed to a 10/30 standard taper inner joint. In all cases the tubes were either sealed off after evacuation (contents cooled in liquid nitrogen, if necessary), or were capped with a standard taper joint containing a stopcock. The 3 mm EPR tubes typically were charged with about 1 mmol of NP.

4. General procedures: A seamless stainless steel dry box was used for handling liquid and solid materials, and for storage of reactors and infrared cells where this was feasible. The box was purged continously with dry air (<1 ppm H_2O in, typically 2-3 ppm H_2O out).

NP fluff was employed in a majority of the experiments. Unless otherwise specified the fluff had been dried by evacuation at $\lesssim 10^{-4}$ mm for 75-80 hours at ambient temperatures. Gaseous reagents were transferred via a vacuum system. All stopcocks and joints were lubricated with Kel-F stopcock grease.

D. Compatibility with High Molecular Weight Materials

One can summarize results in this area with the following statement: we have in no instance observed compatibility which in our opinion is satisfactory from a propellant standpoint. The observed compatibilities are good enough to permit propellant processing without serious apparent deterioration through reaction. Various techniques for measuring and identifying reactions indicate, however, that oxidizer-fuel reactions initiate soon after contact at ambient temperatures (75-78°F), and after a few days delay at 42°F. The delay at 42°F may be more apparent than real, since increased viscosities and lower reaction rates may combine to merely prolong the time required for generation of perceptible quantities of reaction products.

Infrared studies have revealed the following general characteristics of the reaction of NP with the high molecular weight organic materials employed in this program (See Figures 2 and 3; Tables 1, 2, 3 and 4).

The *first new functionality* observed in condensed phases is the *C-NO_2* group, with its strongest characteristic absorbance at 1566-1568 cm^{-1}. With pastes composed of NP-MRPX or NP-Soltrol-200 this band appears immediately in FMIR spectra. Films of the mineral oils over which NP has been dusted do not show the 1567 cm^{-1} band immediately. It is very definitely in evidence after one day, and the absorbance increases for about one week; the band after one week is usually about as intense as the 1470 cm^{-1} band for mineral oil.

The minimum detectable concentration of nitromethane in mineral oil is about 0.1 per cent, and the 1567 cm^{-1} band of nitromethane is as intense as the 1470 cm^{-1} band at about 5 per cent nitromethane. From these values one calculates one C-NO_2 to be present per 60-70 CH_2 groups in the week-old NP-mineral oil samples. This indicates a fairly extensive reaction, more extensive than one expects from reaction with the trace impurity or with the trace reactive functionality. Furthermore, each C-NO_2 group must originally have had a counterpart in perchloric acid or an organoperchlorate; neither of these qualify as stable and unreactive.

No evidence of a decrease in C-NO_2 absorbance has been observed. The C-NO_2 group is evidently stable toward NP and its products of reaction with organic fuels.

The C-NO_2 functionality was uniformly observed in all systems in which NP was contacted with liquid hydrocarbons or with the binder in process of curing. These systems are NP-Soltrol-200, NP-Soltrol-200-Vistanex, NP-MRPX, NP-MRPX-UTREZ, and NP-MRPX-UTREZ-NTEB. By way of contrast, the volatile hydrocarbons (See Table 4) yielded only trace quantities of volatile nitroorganic products on contact with NP. This may be due to the relatively low volatility of nitroalkanes, and to physical adsorption on NP. In connection with the latter possibility, C-NO_2 containing products remained concentrated in the vicinity of the solid phase in systems such as NP-MRPX.

Nitric acid is another initial reaction product. It is observable both in the gas phase and in condensed phases.

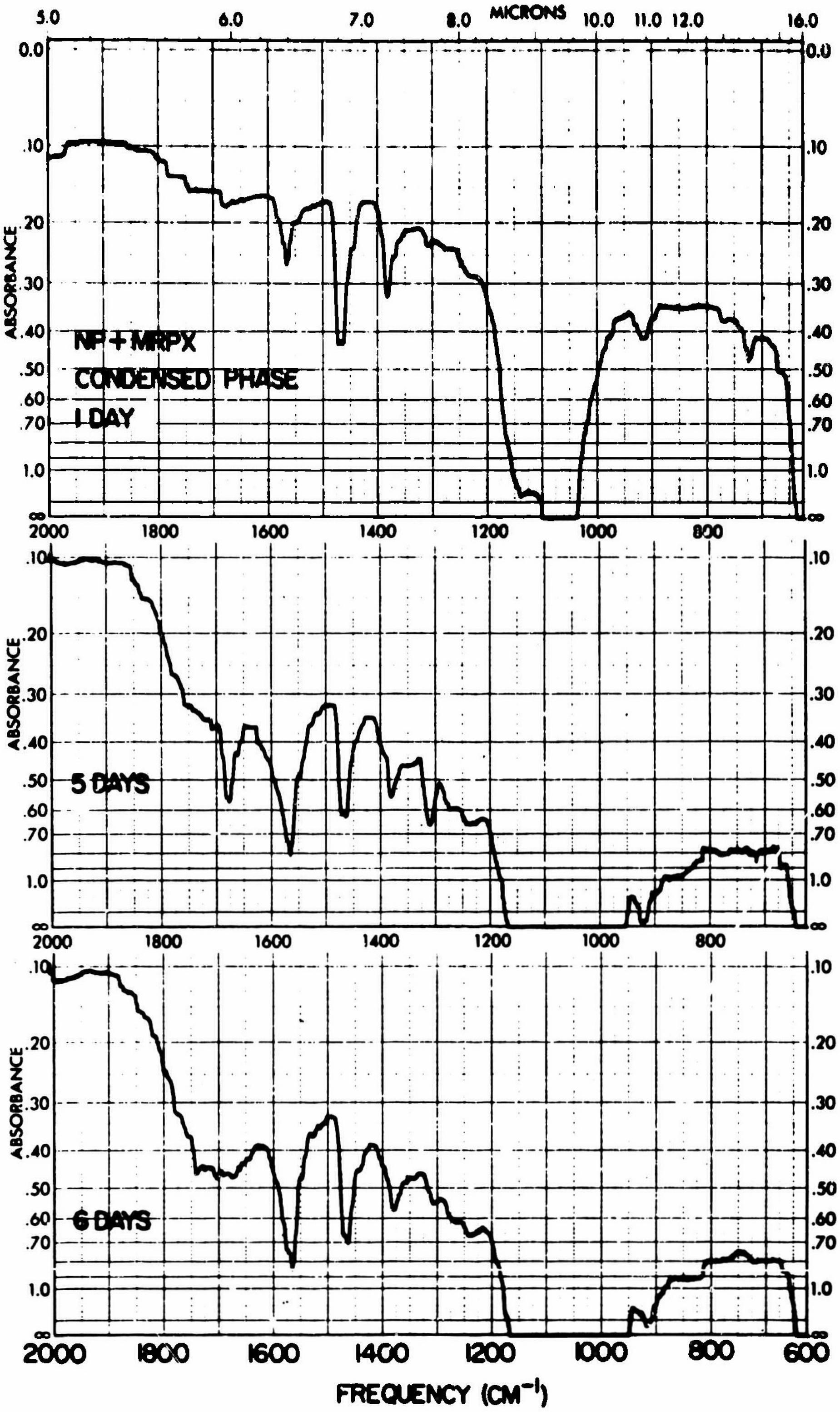


Figure 2 - FMIR Spectra: NP + MRPX

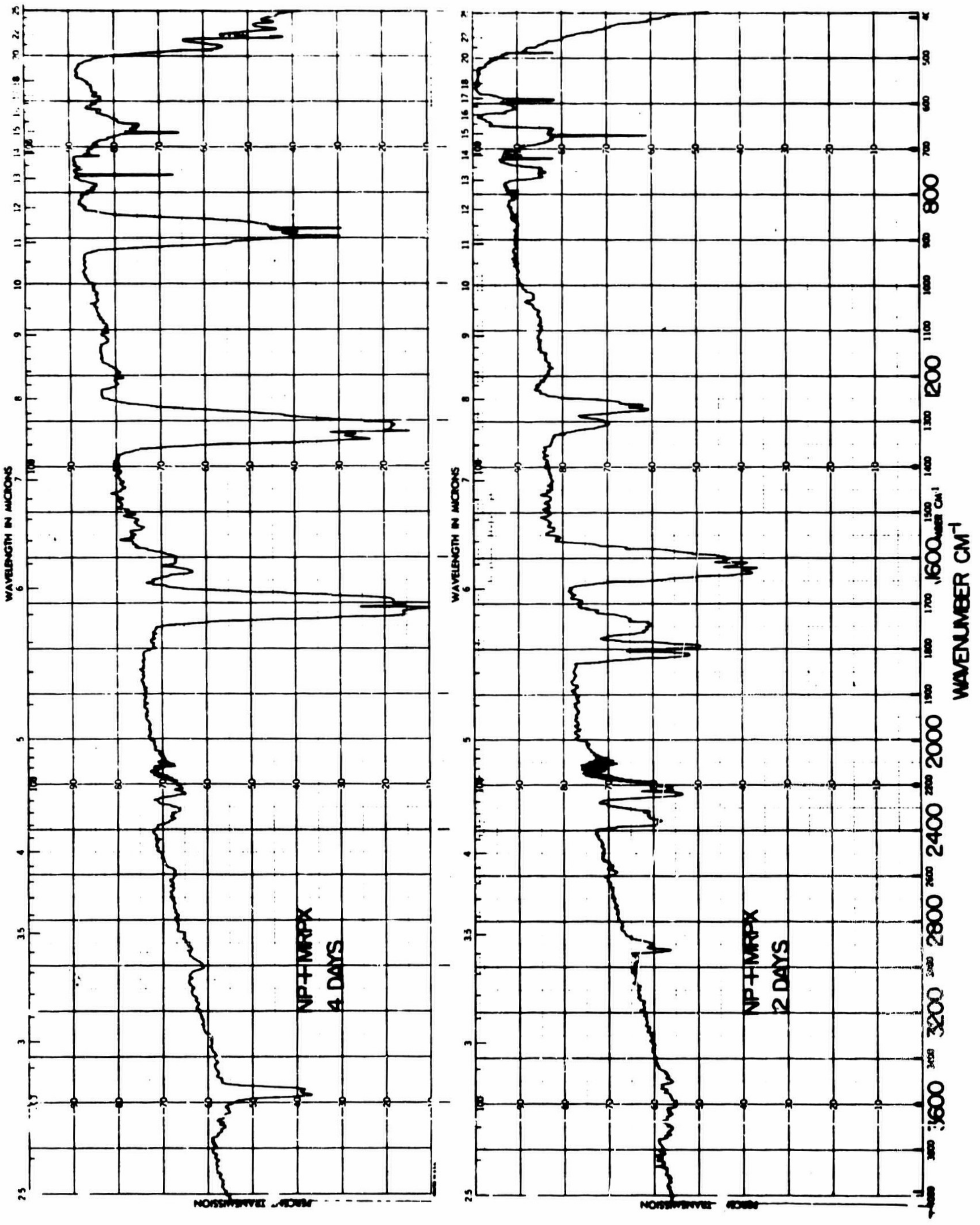


Figure 3 - Infrared Spectra: Gas Phase Over NP + MRPX

TABLE 1

REFLECTANCE INFRARED SPECTRA, RELATIVE INTENSITIES*, NP PLUS MRPX

	Elapsed Time (days)	"H_2O", (1660 cm.$^{-1}$ - 1700 cm.$^{-1}$, vb)	C-NO_2 (1567 cm.$^{-1}$)	-ONO_2 (1680 cm.$^{-1}$)	-ONO_2 (1310 cm.$^{-1}$)	ClO_4 (1070)
Dried NP	1	-	30	-	-	vs,b
	2	Weak	50	15	10	"
	5	Medium	125	80	50	"
	6	Medium	125	--	--	"
Undried NP	1	Weak	50	20	10	"
	2	Medium	90	90	40	"
	3	Medium	150	120	60	"
	4	Medium	200	200	90	"
	7	Strong	150+	-	-	"

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* Intensities relative to 100 for the 1470 cm^{-} band of MRPX.

Note: With elapse of time the base line shifted downward at shorter wave numbers so that near the end of the experiments radiation of 1200 cm.$^{-1}$ or less was nearly completely absorbed.

TABLE 2

INFRARED SPECTRA, RELATIVE INTENSITIES*
NP-UTREZ-MRPX; NP-UTREZ-MRPX-NTEB

	Days	Water (1660-1700 cm.$^{-1}$)	C-NO_2 (1567 cm.$^{-1}$)	-ONO_2	ClO_4 (1100 cm.$^{-1}$)	$\equiv NNO_2^+$ (1700 cm.$^{-1}$)
NP-UTREZ-MRPX	1	m	(100)	-	vs,b	
	5	ms	(100)	-	vs,b	
NP-UTREZ-MRPX-NTEB	1	- - - - -	No Change	- - -	- - -	- - -
	2	- - - - -	No Change	- - -	- - -	- - -
	4			ca. 1560w	w	(10)
	7		(5)	1650-1690(20)	w	(30)
	8		(5+)	1675(50) 1310(50)	s vs	(40)
	9		(10)	1285-1310(15) 1675(?)	vs	(60)
	17		20	?	vs	80
	28	- - - - -	No Change	- - -	- - -	- - -

---

* Intensities referred to 100 for 1470 cm.$^{-1}$ band.

TABLE 3

INFRARED INVESTIGATIONS, INTERNAL REFLECTOMETRY

System	Observations
NP-UTREZ-NTEB-MRPX, stored at 42°F	General behavior similar to that of the same system stored at ambient temperatures, except that little reaction occurred in 21 days, and slow but steady reaction took place for next 28 days.
NP-MRPX, stored at 42°F	Slow reaction: 2 - 3 days at 75 - 78°F equivalent to 14 - 17 days at 42°F.
NP + Cyclohexylpiperidine in CCl_4	Examined wet solid phase periodically. $-ONO_2$ strong in 1 day; $C-NO_2$ medium in 3 days, strong in 7 days; possible carbonyl group; no evidence of $\equiv NNO_2^+$.
NP + NTEB in CCl_4	Examined wet solid phase periodically. NTEB concentrated in solid phase. $-ONO_2$ weakly evident in one day, and possible $C-NO_2$. Spectra varied thereafter, but inconclusive about nature of change. No evidence of $\equiv NNO_2^+$.
MRPX + NP treated in CCl_4 with hexamethylenetetramine	Reacted as with untreated NP -- no reduction in rate.
#5 Reta-coated NP #5A Reta-coated NP #5 Reta-coated NP + MRPX	Saw only NO_2^+, ClO_4^-. NO_2^+, ClO_4^-, weak $-ONO_2$. IR changes about 50% as extensive as with NP fluff-MRPX in identical time periods
NP(BF_3 treated) + MRPX	No $-ONO_2$ observed, otherwise results comparable to untreated NP.
NP-MgO(10%) + MRPX	$C-NO_2$ strong in 3 days; strong absorbance at 1710 cm.$^{-1}$ (carbonyl ?); Possible $RONO_2$-, strong absorbance at 1640 cm.$^{-1}$, shoulder at 1275 cm^{-1}.
NP (excess) + 1% cyclohexylpiperidine in CCl_4, periodically removed wet solid phase for FMIR	Band at 1460 cm.$^{-1}$ typical of CHP increased over 3 day period, then remained constant. After 1 day, bands at 1310 cm.$^{-1}$ and 1675 cm.$^{-1}$ were of medium intensity, and increased to about the 3rd day. A weak peak appeared at 1750 cm.$^{-1}$ on 3rd day, remained constant thereafter. $C-NO_2$ (1567 cm.$^{-1}$) weakly evident on 3rd day, strong after 7 days, and of constant intensity after about 10 days.
NP-SiO_2 + MRPX	Results qualitatively the same as with NP treated with BF_3.

TABLE 4

RESULTS OF INFRARED INVESTIGATIONS IN GAS CELLS*

System	Time (days)	Observations	Remarks
NP-MRPX	0	HNO_3, 0.5 mm.	HNO_3 evolves initially, then dissappears as NO_2, N_2O and CO_2 become major products. NOCl a minor product.
	1	HNO_3, 1 mm.	
	4	HNO_3, 7-8 mm. CO_2, N_2O	
	7	HNO_3 gone N_2O and CO_2, 3-5 mm. NOCl, 0.1 mm. NO_2, 5-7 mm.	
	12	No HNO_3 N_2O, NO_2, CO_2 10-15 mm. NOCl, 0.5-1 mm.	
NP-MRPX-C_3H_8	0-12		Product distribution and chronology very similar to NP-MRPX. No precepitible consumption of propane.
NP-MRPX-UTREZ-NTEB	29	N_2O-trace	System cured six days before start of run. Gas breakthrough evident in about one month. Evolved gases chiefly N_2O and CO_2.
	38	N_2O + CO_2-trace	
	49	N_2O, CO_2, NO_2Cl	
	57	N_2O, 10 mm. CO_2, 10-15 mm. NO_2Cl, 1 mm.	
Undried NP fluff, glass frit between cell and side arm	0	HNO_3, 0.5 mm.	HNO_3 observed initially, increased in quantity over about 1 week; NO_2^+ and ClO_4^- deposited on cell windows; all NO_2^+ and majority of ClO_4^- removed by hydrolysis.
	1	HNO_3, 0.6-0.7 mm. NO_2^+, ClO_4^-, weak	
	7	HNO_3, 1.0-1.5 mm. NO_2^+, ClO_4^-, strong	
Removed NP, exposed cell to H_2O vapor, evacuated	8	ClO_4^-, about 30% of intensity before hydrolysis	
Dried NP	32	HNO_3 ca. 0.1 mm. ClO_4^-, trace	
Reta-coated NP #5			Solid sampler holder; observed no bands other than those for NO_2^+ and ClO_4^-.

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* Solids and liquids placed in a side arm; spectra of gases and deposits on cell windows (AgCl) observed; pressures approximate.

TABLE 4 (Continued)

System	Time (days)	Observations	Remarks
NP + hexane (30 mm)	0	No rxn	Reaction evident in one day. Major products are NO_2Cl, HNO_3, CO_2 and N_2O
	1	NO_2Cl, 2 mm HNO_3, 5 mm	
	4	NO_2Cl, 5 mm HNO_3, 20 mm CO_2, 3 mm N_2O, trace $COCl_2$, Trace	
	8	NO_2Cl, 15 mm HNO_3, 35 mm CO_2, 12 mm N_2O, 5 mm	
NP + isooctane (35 mm)	0	No rxn	Products and reaction rates similar to those of NP + hexane
	1	HNO_3, 5mm NO_2Cl, 1 mm NO_2^+, ClO_4^-, weak	
	4	NO_2Cl 5 HNO_3 25 CO_2 5 N_2O, 2 No NO_2^+, ClO_4^-	
	11	NO_2Cl, 15 mm HNO_3 15 mm CO_2 30 mm N_2O, 25 mm NO_2, 5 mm	
NP + pentane (40 mm)	0	No rxn	Reaction slower to initiate than with hexane and isooctane
	3	HNO_3, 0.25 mm NO_2Cl, trace	
	10	NO_2Cl, 10 mm HNO_3 20 mm N_2O, trace CO_2, 3 mm NO_2^+, ClO_4^-, weak	
	40	HNO_3, 40 mm NO_2Cl, 20 mm N_2O, 5mm CO_2, 45 mm $R-NO_2$, 1 mm $COCl_2$, 1 mm	

TABLE 4 (Concluded)

System	Time (days)	Observations	Remarks
NP-CH_4	35	HNO_3, ca. 0.3 mm. NO_2^+, ClO_4^-, weak	No products expected of CH_4 oxidation.
NP-C_2H_6	4	HNO_3, ca. 0.1 mm.	No products expected of C_2H_6 oxidation.
	11	HNO_3, ca. 0.3 mm. ClO_4^-, weak	
	34	HNO_3 ca. 1.5 mm. NO_2^+, ClO_4^-, medium	
Evacuated cell	35	No HNO_3 NO_2^+, ClO_4^-, unchanged	
	46	HNO_3, ca. 0.1 mm.	
NP-$(CH_3)_4C$	1	HNO_3, trace NO_2^+, ClO_4^-, weak	No oxidation products of $(CH_3)_4C$ observed. NO_2Cl formed in small amounts (ca. 1 mm.).
	4	No change	
	11	HNO_3, 0.2 mm. NO_2^+, ClO_4^-, weak	
	18	HNO_3, 0.5 mm. NO_2^+, ClO_4^-, medium-weak	
	26	HNO_3, 0.5 mm. NO_2^+, ClO_4^-, medium	
	35	HNO_3, 2 mm. NO_2^+, ClO_4, medium-strong	
NP-CH_3Cl and NP-C_2H_5Cl			HNO_3 observed at 0.3-0.5 mm. within one day, and pressure increased to 3-4 mm. in 4 days. NO_2^+ and ClO_4^- deposited cell windows after one day. NO_2Cl produced in relatively large quantity.

The identification of nitric acid in condensed phases by FMIR spectroscopy is less positive than we wish. The two observed frequencies occur at 1680 cm^{-1} and 1308-1310 cm^{-1}. The 1310 cm^{-1} band is essentially correct for nitric acid, but the companion band should occur at 1710 cm^{-1}. A band at 1680 cm^{-1} fits an organonitrate, but its companion band should occur at about 1280 cm^{-1}. The two observed frequencies are close to those observed by Callery Chemical Company (Ref. 6) for $HNO_3 \cdot 2HClO_4$ at low temperatures, and it is possible that the 1680-1310 cm^{-1} combination is typical of nitric acid adsorbed on NP. In any event, gaseous nitric acid is very definitely observed, and for this reason we are strongly inclined to assign the 1680 and 1310 cm^{-1} bands to nitric acid retained in condensed phases in the immediate vicinity of the oxidizer.

Nitric acid is unique in that it increases in quantity, both in gaseous and condensed phases, and then rather abruptly disappears. In the condensed phase the disappearance is not accompanied by a definite appearance of new IR active species. In the gas phase, on the other hand, one sees NO_2 as the apparent replacement product. The time of nitric acid disappearance is also approximately the time that CO_2 and N_2O become detectable products.

In condensed phases, the other major change in infrared spectra consists of the growth of a very broad absorbance extending from about 1650 cm^{-1} to 1800 cm^{-1}. Maximum absorbance normally occurs at about 1700 cm^{-1}. This broad band is similar in appearance to a broad band observed by Callery Chemical Company (Ref. 6) for $HNO_3 \cdot 2HClO_4$ at -42°C. The absorbance also occurs at about the frequency of water of solvation, and this fact led us to believe originally that we were seeing water absorbed in a highly polar region created by reaction products concentrated near the oxidizer surface. The "water" hypothesis we now are not inclined to believe--water even in a solvated form is hard to accept in an NP system. In this general region of the infrared (1650-1800 cm^{-1}) several functional species absorb strongly, namely carbonyl groups, organonitrates, nitric acid, nitrogen oxides, nitryl chloride, and other N-O species. In lieu of a more definite explanation, it is suggested that the broad band is due to the presence of several of these species, that bands for individual functionalities are likely broadened in the liquid phase, and that resolution into distinct bands is thus possible only when a particular species is present in relatively high concentration. The 1680 cm^{-1} band attributed to nitric acid does in fact project out of the broad band.

Such an interpretation helps to explain the fact that the only oxidized or reacted organic materials identified with certainty are carbon dioxide and nitroalkanes. Carbon dioxide appears only after a relatively long time interval, a time interval during which overall reactions are extensive. No partially oxidized species such as organic acids, esters or acid anhydrides have been detected with certainty. Surely some intermediate C-O species are formed; we feel that they are, and that they contribute to the broad infrared absorbance at 1650-1800 cm^{-1}.

<u>Carbon dioxide</u>, <u>nitrous oxide</u>, <u>nitrogen dioxide</u>, and <u>nitrosyl chloride</u> appear in the gas phase after time intervals ranging from 3-4 days to about a month. The shorter time interval applies to a system such as NP-MRPX, and the longer interval to the complete binder system. Carbon dioxide and nitrous oxide are the only volatile compounds detected by infrared above the complete binder system. Nitric acid is a condensed phase product in the complete binder system, but it apparently is consumed by oxidation reactions rather than evolved into the gas phase. Nitrogen dioxide has not been identified in any condensed phase; we interpret this to mean that NO_2 is not appreciably soluble in liquid phases, does not absorb strongly (as HNO_3 apparently does) on solid phases, and that the MIR method is incapable of resolving NO_2 in the concentrations extant in condensed phases. In other words, we believe NO_2 to be a significant intermediate, but one which reacts further if trapped in a polymeric system.

<u>The apparent sequence of reactions</u>--the data are susceptible to treatment in this manner, but one must bear in mind that substantial gaps still exist--several intermediate products have not been identified. The sequence we have observed is as follows:

(a) R-NO_2 and HNO_3 are initially observed products. The nitroalkane functionality increases in concentration for a period of time, but its concentration eventually appears to maximize.

(b) Nitric acid increases in quantity for a time, then rather abruptly disappears. In fluid systems NO_2 appears in the gas phase approximately when nitric acid disappears. The quantity of NO_2 increases to a fairly constant value.

(c) N_2O and CO_2 are minor products at the time of nitric acid consumption and NO_2 generation. The N_2O and CO_2 then increase in quantity during runs of several weeks duration.

This sequence of events implies that initial reactions are relatively simple, consisting perhaps of replacement of C-H by C-NO_2 and generation of $HClO_4$ which decomposes or reacts with organic substances. Nitric acid in this scheme is a by-product, one which results from generation of water which hydrolyzes NP. During this initial period little or no carbon dioxide is produced, and the system remains compatible with nitric acid. This compatibility decreases as oxidative reactions increase in complexity until nitric acid is no longer compatible. From thenceforth the fuel scavenges oxidizing oxygen almost at will from oxides and oxyacids of chlorine and nitrogen, and reactions become autocatalytic in nature.

The results support a conclusion one no doubt should intuitively assume, namely that a little reaction involving NP is likely to be followed by further and more diverse reactions, and that compatibility will deteriorate rather than improve with time. The deterioration in compatibility appears to be a function of both of a buildup of diverse oxidizing species, and of an increasing oxidizability on the part of the fuel.

1. Comparative compatibilities: This discussion applies still to higher molecular weight materials. NP appears to be a good leveling agent, in that significant differences in reactivity, as measured by FMIR, were not detected for several reactants. Soltrol-200, MRPX, soltrol-200 + Vistanex, and MRPX + UTREZ reacted at about the same rates with dried NP fluff. Undried NP fluff was distinctively more reactive than dried fluff. This fact corroborates observations made elsewhere, emphasizes the need for dry NP and dry binder constituents, and is another reason why it is important that the initial reaction between NP and binders be eliminated.

The best compatibility was observed with the complete binder system, NP-MRPX-UTREZ-NTEB. This result has been observed at the United Technology Center (Ref. 1), where it was also found that addition of cyclohexylpiperidine, CHP, improved compatibility. These observations suggest that amines are able to passivate NP in some manner. One possible mode of passivation is suggested by the work of Olah (Ref. 9), who found that NO_2^+ ion adds to the nitrogen atom of pyridine, and a nitroaminonium anion results.

NTEB contains four tertiary nitrogen atoms; three of the four are converted to secondary amines by the polymerization reaction. There is the possibility then that the NO_2^+ ion of NP adds to amine nitrogen atoms in NTEB, and that the surface of NP is thus coated with a new perchlorate of diminished reactivity. A second possible mode of passivation consists of neutralization of nitric and perchloric acids. Both modes could of course operate simultaneously.

Observations of the complete binder system by FMIR support the "NTEB·NO_2^+" mode of passivation. Three to four days after preparation of the formulation a new IR active species appears. The new absorption first appears as an apparent shoulder, at 1700-1715 cm^{-1}, on a strong band of NTEB at 1740 cm^{-1}. After seven days the new band peaks sharply at 1705 cm^{-1} and is more intense than the 1740 cm^{-1} band. After about two weeks the 1705 cm^{-1} band is more intense than any other in the spectrum with the exception of the 1070 cm^{-1} band for the perchlorate ion (the 1070 cm^{-1} band is very broad and strong after 8 - 10 days).

Olah has attributed an infrared band at 1705 cm^{-1} to the nitropyridinium ion, and it is thus reasonable to postulate that the same band in our system is due to "NETB·NO_2^+". This assignment must be viewed as tentative, particularly since we have no supporting evidence.

In complete systems the 1705 cm^{-1} band appears to slightly precede other bands attributable to reaction products, though for the most part C-NO_2, HNO_3 and "NTEB·NO_2^+" develop together. The time required for reaction of approximately the same extent are 2 - 4 days in the absence of NTEB, and 8 - 12 days in the presence of NTEB. Nitric acid disappears abruptly in the complete system as it does in systems which do not contain NTEB.

Reduced temperatures are also effective in lowering reaction rates. The temperature effect is in fact much more pronounced than the effect of NTEB. Two to three days at 75 - 78°F is equivalent to 14 - 17 days at 42°F, with NP-MRPX; at 42°F, HNO_3 is never in evidence as a distinct species, and the comparison of rates is based on the intensities of bands for C-NO_2, perchlorate, and the broad band at 1650 - 1800 cm^{-1}. With NP in the complete binder system, FMIR evidence of reaction does not appear for about three weeks. A small peak at 1567 cm^{-1} (C-NO_2) is present initially, but remains unchanged in intensity over the three-week interval. The generation of this initial quantity of C-NO_2 likely occurred during the few hours required for sample preparation and obtaining the original spectrum. From 3 to 7 weeks, C-NO_2, "NTEB·NO_2" and perchlorate absorptions increased, and the band at 1680 cm^{-1} (HNO_3) also appeared.

The complete system at 42°F appears to require an initiation or induction period. Perhaps low temperature and the passivating effect of NTEB combine to essentially halt reaction. It is apparent, however, that some reaction does occur during the induction period, and a cumulative effect eventually results in a breakdown and relatively extensive propagation of reaction.

One other fact is obvious in the complete system at 42°F, namely that the infrared absorption due to the perchlorate ion or group remains fairly constant during the induction period, and becomes quite strong when bands for C-NO_2, etc. begin to increase in intensity. In all the systems observed with FMIR, perchlorate absorption has eventually become very strong, but in few has there been clear cut evidence that intensification of the perchlorate band is dependent on the development of other product species. Intensified perchlorate absorption could obtain either from physical processes, such as gravitational settling of particles, or from chemical processes which give ClO_4 freedom of movement it doesn't possess in NO_2ClO_4. Perchloric acid, for example, can move about with relative ease, and generation of perchloric acid would explain the development of very intense absorption in the 1100 cm^{-1} region.

The fact that undried NP is more reactive than dry NP has been mentioned earlier in this report, has been observed elsewhere, and needs no amplification save for restatement for emphasis; the effect is very real, and dryness is both necessary and desirable.

A few pretreatment techniques were studied briefly in an effort to reduce reactivity. These treatments were screened by FMIR with the NP-MRPX systems. The BF_3 treatment was not effective, nor were additions of ultra-dry, finely divided silica and magnesia. Silica was looked upon as a possible water scavenger. With magnesium oxide it was hoped that neutralization of acids would minimize reactivity.

$$HNO_3 + HClO_4 + 2MgO \longrightarrow MgOH(ClO_4) + MgOH(NO_3)$$

Neither treatment was detectably beneficial. NP treated in carbon tetrachloride with cyclohexylpiperidine was no less reactive than untreated NP.

2. Compatibility of NP with amines: Since NTEB and cyclohexylpiperidine (Ref. 1) appear to passivate NP, some time was spent looking at the compatibility of these two amines and of hexamethylenetetramine with NP. We were specifically interested in ascertaining whether adverse reactions occurred. The amines and NP were contacted in carbon tetrachloride to minimize the possibility of spontaneous reaction and to afford the opportunity for slow and ordered reaction and/or adsorption.

Of the three amines, only cyclohexylpiperidine was completely miscible with carbon tetrachloride. An EPR sample soon gave a very pronounced ClO_2 signal, and FMIR spectra showed reaction to be extensive in 1 - 2 days. The FMIR spectra did not contain the 1705 cm^{-1} band expected for "$CHP \cdot NO_2^+$", and exhibited strong covalent nitrate and nitroalkane bands along with a slowly developing band at 1750 cm^{-1} due perhaps to C=O.

Hexamethylenetetramine was insoluble in and lighter than carbon tetrachloride, so no IR studies of the $HMT\text{-}NP\text{-}CCl_4$ were attempted. In an EPR tube, this system slowly developed a strong ClO_2 signal.

Studies of NTEB yielded fairly inconclusive results. FMIR spectra of the solid phase of $NP\text{-}NTEB\text{-}CCl_4$ gave no evidence of "$NTEB \cdot NO_2^+$". The NO_2^+ and ClO_4^- ions were observed, as was adsorbed NTEB. In initial spectra covalent nitrate absorbed weakly, but as time progressed the only change consisted of increased absorption of radiation at wave numbers higher than 1600 cm^{-1}. EPR spectra of this system revealed a moderate concentration of ClO_2.

Cyclohexylpiperidine and hexamethylenetetramine unquestionably react adversely with NP in carbon tetrachloride. In a binder system the adverse reactions may be minimal, but one would not predict lasting or permanent passivation. The results with NTEB indicate a compatibility with NP consistent with passivation, but permanent passivation does not appear to be indicated.

E. Compatibility with Volatile Hydrocarbons

These studies were undertaken to determine if possible the fundamental, relatively long term (1 - 2 months) compatibility of NP with simple hydrocarbons. The non-simple (high-boiling, sometimes polymeric) organic materials discussed in II-D are obviously not sufficiently compatible with NP. The high boiling substances are inherently difficult to dry and free of trace reactive functionalities. They also are inherently diverse in structure -- a straight chain mineral oil will contain some branching, for example, and as a consequence NP will see several types of C-H and C-C bonds which may vary in reactivity. Development of the United Technology Center binder required painstaking attention to structure, purity, and processing conditions. The materials we have investigated are therefore among the best available, and it is very appropriate to ask the question: What is the inherent compatibility of NP with hydrocarbons? This question is particularly appropriate when one considers the fact that present developmental efforts involve NP-fuel contact; NP is either used "raw" or is covered with a protective organic-based polymer (notably the Reta polymers).

We have endeavored to answer this question. The results are not free of ambiguity, and our answer is not as completely definitive as desired. We have, however, obtained results which illustrate the severity of the problem and may, if one is so inclined, be used as the basis for discarding NP as an oxidizer for solid propellants.

1. Isooctane, n-pentane, and hexane: These hydrocarbons were pretreated in two ways. The first consisted of drying over sodium aluminumhydride. In the second method the hydrocarbons were dried as above, contacted as gases with NP for two days, scrubbed with dilute caustic to remove acid gases (HNO_3, NO_2Cl, CO_2 and NO_2), and redried. The second method was employed to hopefully remove the "trace reactive impurity."

The hydrocarbons were contacted with NP either in infrared cells or in flasks from which samples were withdrawn periodically. In all cases except one (a run with isooctane) the hydrocarbons were entirely in the gas phase at 30 - 50 mm. pressure. In all the experiments reaction was evident after about one day, and thereafter proceeded slowly but surely toward complete oxidation of the hydrocarbon. All runs were allowed to continue to the point of generation of about one mole of carbon dioxide per mole of initial hydrocarbon, and a few continued until very little hydrocarbon was detectable by infrared. Pretreatment with NP (method two above) may have reduced initial reactivity slightly. Complete oxidation required six weeks to two months, so reactions are by no means spontaneous. They are impressive, however, for their assuredness.

The manner of reaction between NP and isooctane, n-pentane and hexane is as follows (see Table 4, Figure 4). Nitric acid is the first observed product, but it is followed closely by nitryl chloride. These two products increase in concentration at approximately equal rates. After 3 - 6 days carbon dioxide and nitrous oxide are observed; both increase steadily in quantity thereafter. Phosgene is a very minor product, and a trace of R-NO_2 (1567 cm^{-1}) appears in the gas phase after reaction has been extensive.

In only one other type of system (C_2H_5Cl, CH_3Cl: see E-2) was nitryl chloride observed as a major and initial product. The observation of nitryl chloride could be construed as evidence that oxygen atoms are stripped directly from the perchlorate ion.

$$NO_2ClO_4 + \text{fuel} \longrightarrow NO_2Cl + \text{oxidized fuel}$$

This is considered to be unlikely. It is felt that attack of fuel by the nitronium ion results in conversion of ClO_4^- to a covalent state, e.g., perchloric acid or an organo perchlorate, which is highly oxidizing. Nitryl chloride then forms by side reactions which are not immediately obvious.

One fact is worthy of note. The initially observed nitrogen bearing products (HNO_3 and NO_2Cl) are in the +5 oxidation state. Oxidation of fuel has thus been chiefly effected by the perchlorate group during early stages of reaction. In advanced stages of reaction N_2O becomes a major product, and reduction of N-O species becomes significant. The perchlorate ion is therefore a major contributor to reactions, even though its involvement may not be entirely voluntary.

Nitrogen dioxide was seldom an observed product with this series of hydrocarbons.

2. <u>Methyl chloride and ethyl chloride</u>: Attempts to define the long-term compatibility of these chloroalkanes were frustrated by the ability of the gases to permeate Kel-F stopcock grease. Sealed tubes are apparently required. Nevertheless, NP-RCl systems were observed for 2 - 3 weeks and found to be qualitatively less reactive than pentane, hexane and isooctane, but more reactive than propane and ethane. Nitric acid and nitryl chloride

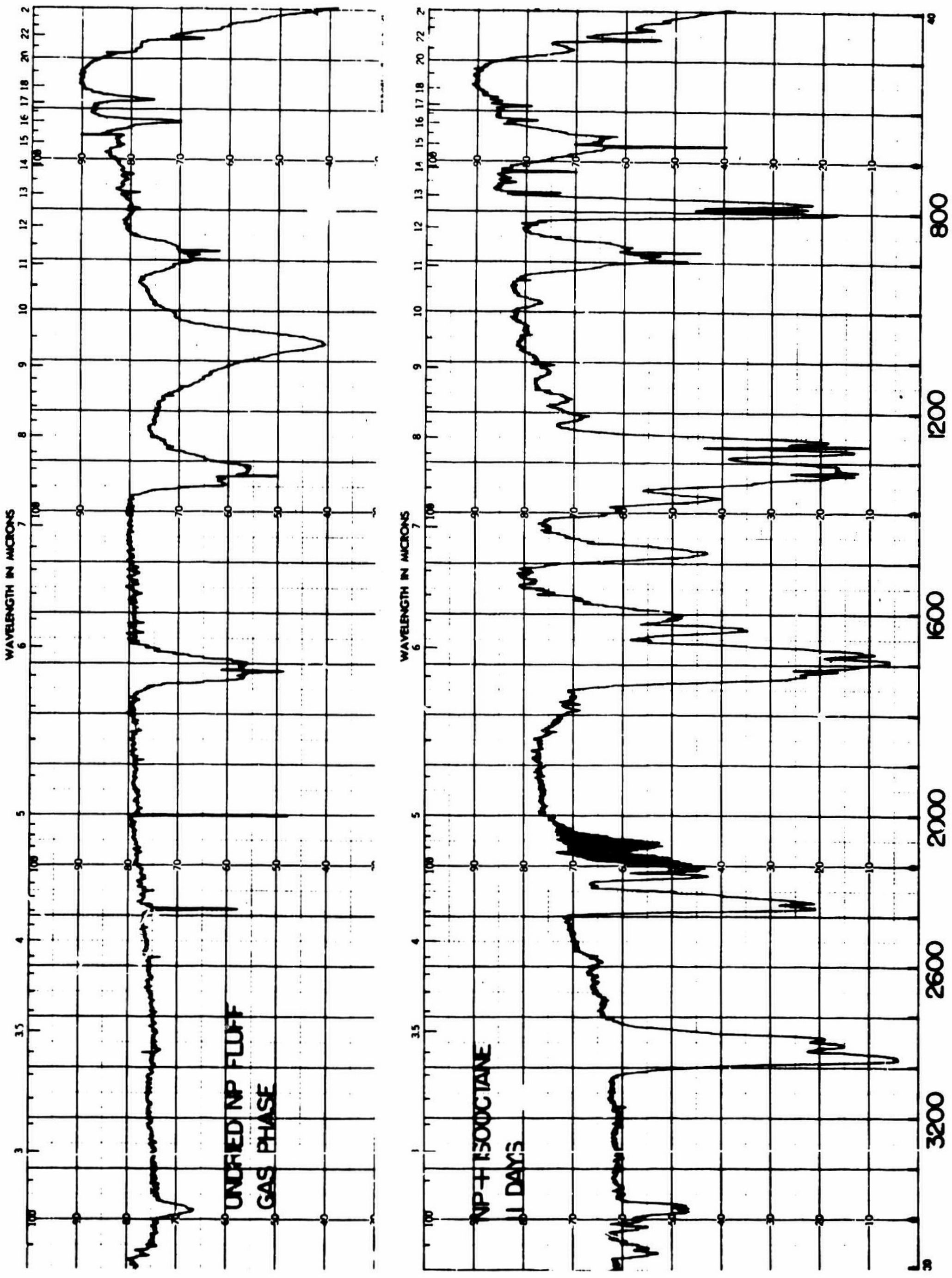


Figure 4 - Infrared Spectra of Gas Phase Over Undried NP, and of Gas Phase with NP + Isooctane

were the chief volatile products, and nitronium perchlorate volatilized readily to windows of infrared cells. We are not well pleased with the quality of the data on methyl chloride and ethyl chloride, but are confident that it has been shown that substitution of chlorine for hydrogen will not universally improve compatibility. One concludes that dipole effects due to the chlorine atom increase the reactivity of remaining C-H bonds in methyl chloride and ethyl chloride. The effect may well be the reverse in other organohalides, however, as in chloroaromatics.

3. Methane, ethane, propane and neopentane: Studies with these compounds have been quite frustrating in that we have been unable to our satisfaction to differentiate between the very slow reaction and phenomena attributable to NP proper. Methane has been given a clean bill of health; at ambient temperatures significant evidence of reaction was not detected, in experiments lasting as long as two months, by EPR and infrared. With ethane, propane, and neopentane the observations were as follows: Over periods of several weeks nitric acid was slowly evolved into the gas phase. The partial pressures of nitric acid were only about 2 - 3 mm., so total evolved quantities were low. The second change was the deposition of the NO_2^+ and ClO_4^- ions on infrared cell windows; volatilization of NP therefore was affected. Traces of NO_2Cl were sometimes observed; the NO_2Cl may have originated from reaction of NP with silver chloride windows, or from organic-NP reactions. No carbon dioxide was detected by infrared, and involvement of hydrocarbons in reactions was so slight (if any) that no net change in partial pressure was observed. The same systems in EPR tubes generated ClO_2 in concentrations well above concentrations found in dried NP. The ClO_2 concentrations were not, however, high enough that one could conclude that reaction was extensive. One exception is unfractionated propane; in spite of purity reportedly equal to or better than 99.97 per cent, untreated propane and dried NP generated ClO_2 in substantial concentrations.

The above results can be interpreted in three ways, or in combinations thereof: (1) ethane, propane, and neopentane are several orders of magnitude more compatible with NP than pentane, isooctane, and hexane, but reaction nevertheless does proceed at a measurable rate and in a manner typical of the first stages of reaction with pentane, etc.; (2) trace impurities in the hydrocarbons are chiefly responsible for the observed phenomena; and (3) NP reacts with water which is extracted from glassware or which slowly diffuses through joint lubricant. Part of the nitric acid generated by hydrolysis evolves into the gas phase. Some perchloric acid also volatilizes, and reacts with nitric acid to reform NO_2ClO_4.

$$2H_2O + 2NO_2ClO_4 \longrightarrow 2(HNO_3 - HClO_4)$$

$$\downarrow$$

$$H_3OClO_4 + NO_2ClO_4 + HNO_3$$

$$H_3OClO_4 + NO_2ClO_4 \rightleftharpoons HNO_3 + 2HClO_4$$

These equations appear to fairly accurately describe the hydrolysis of NO_2ClO_4 (Ref. 6). Two moles of water should generate one mole of free nitric acid which should appear in the gas phase save for that absorbed on the solid phase. The mixture of H_3OClO_4 and NO_2ClO_4 is slightly volatile, apparently via the depicted equilibrium, and this provides a mechanism for volatilization of NO_2ClO_4.

Experiments with methane-NP, and blanks with NP in the infrared cell discount the possibility that water contained in the apparatus is solely responsible for nitric acid and volatilized NO_2ClO_4. The blanks and methane-NP yielded the same products, but to a much smaller extent over comparable lengths of time than did C_2H_6-NP, C_3H_7-NP, and $(CH_3)_4C$-NP. Ethane, propane, and neopentane were therefore either less dry than methane, or were slightly reactive. Water contained in the reactants would, we believe, be evidenced by nitric acid at a definite and unchanging pressure, as opposed to the steadily increasing pressure observed with ethane, methane, and neopentane. The same argument applies to trace impurities--these should react quickly to produce a definite quantity of nitric acid. The above arguments must be accepted only with reservation, since small changes have been compared with other small changes. We conclude, nevertheless, that ethane, propane, and neopentane do indeed react with NP, albeit very slowly.

The practical implications of the experience with the simplest hydrocarbons are less ambiguous than the fundamental question of reactivity. One can conclude without ambiguity that nitric acid will be ever present in practical NP-containing systems, that perchloric acid will also be present, and that nitronium perchlorate will in effect be volatile. The generation of quantities of ClO_2 accompanying contact of NP with pure, simple hydrocarbons surely means that a situation of instability and reactivity has been created. The experiments are practically useful, therefore, if for no other reason than that they clearly show that these evidences of reactivity and instability are difficult to avoid even with the rigor of treatment possible in the laboratory. It is therefore not surprising that the lower-purity, more diversely structured constituents of a binder exhibit a much higher degree of reactivity.

F. Reta-coated NP

Two samples of Reta-coated NP were studied. The samples were old, and had been found unsuitable (reactive) at the United Technology Center. They do not therefore qualify as representative samples. Our observations are reported with this reservation.

Both samples were examined by infrared and EPR. The more reactive sample exhibited only the infrared bands typical of NO_2^+ and ClO_4^-. The less reactive sample exhibited the same bands, and in addition gave a weak absorption at about 1700 cm^{-1} which likely is due to covalent nitrate. Chlorine dioxide was present, by EPR, in both samples at concentrations 50 to 100 times the concentration normally found in NP. A brief FMIR study of the more reactive sample revealed it to be reactive with MRPX.

The results are not a sufficient basis for generalizations about the Reta coating technique. The observations are, however, consistent with the view that NP reacts slowly with the Reta coat. In the two samples, the slow reaction has in our opinion resulted both in destruction of the impermeability of the coating, and in the generation of sufficient nitric acid and perchloric acid to make possible the massive transport of NO_2ClO_4 to the exterior surface of the coating. The latter effect (volatilization) we consider to be by far the most serious conclusion. A slow reaction confined to the NP-coating interface may require a considerable length of time to become of serious consequence. If, however, this reaction affords NP the opportunity to migrate at will, the protective coating no longer serves as a barrier, and reactivity becomes that of NP with the bulk of the binder.

G. The "Volatility" of NO_2ClO_4

This property of NP deserves special mention, since we believe it to be of considerable importance. The fact that acids of hydrolysis are volatile is not new, and the facts of hydrolysis are fairly completely understood. The observations of this program are consistent with current interpretations. No new basic facts have been added, but the volatilization has been seen under somewhat new circumstances, and we wish to interpret volatility in terms of reactivity and compatibility.

We have observed the transport of NO_2ClO_4 through the gas phase, in infrared cells, under the following conditions:

(a) Dried NP: after several weeks, weak peaks for NO_2^+, ClO_4^- and HNO_3 have developed.

(b) Undried: NO_2^+ and ClO_4^- deposit on cell windows within one day, and gaseous nitric acid appears simultaneously. A glass frit was placed between the cell body and a sidearm containing the NP. The NO_2ClO_4 was therefore transported as gaseous species rather than as dust particles.

(c) In all studies of the systems C_3H_7-NP, C_2H_6-NP, and $(CH_3)_4C$-NP, NO_2^+ and ClO_4^- ions werc transported from sidearms and deposited on infrared cell windows. NP-CH_3Cl and NP-C_2H_5Cl behaved similarly.

(d) Weak bands for NO_2^+ and ClO_4^- were occasionally observed with NP-pentane, NP-hexane, and NP-isooctane during the first week. The adsorption bands disappeared with further lapse of time. This behavior is consistent with the higher reactivity of C_5 to C_8 hydrocarbons compared to reactivities of propane, ethane, and neopentane. Perchloric acid was probably too reactive to survive long in the gas phase.

(e) Dried NP was placed in one arm of an "H" apparatus, and MRPX in the other arm. The leg connecting the arms contained a glass frit. The apparatus was evacuated and stored in the dry box for one month. The gas phase then contained CO_2, N_2O and HNO_3. Fuel and oxidizer had therefore established contact through the gas phase. MRPX is undoubtedly slightly volatile at ambient temperatures, so one cannot for certain state that NP was the volatile constituent. We suggest however, that reacti~~on is~~ chiefly due to the volatility of NP in the presence of trace water.

The consequences of "volatility" are fairly obvious. First of all, the acids of hydrolysis are reactive in their own right, particularly perchloric acid. While the pressure of perchloric acid over hydrolyzed NP is low, it still is sufficiently mobile to be able to seek out reactive sites in a propellant. Secondly, NP cannot in practical systems be viewed merely as a solid phase invariant in shape and form. Surfaces of NP particles are mobile rather than stationary. Passivating treatments are not likely to be permanently effective unless the passivating agent is capable of neutralizing acids. Protective coatings will retain their effectiveness only as long as they are impermeable to volatile acids.

H. Electron Paramagnetic Resonance

EPR studies of NP and NP containing systems have yielded information pertinent to the stability of NP and to its compatibility with organic materials. The EPR method has generally given data qualitatively relevant to compatibility. The species detected in NP usually was ClO_2, and as might be expected a quantitative relationship between reactivity and quantity of ClO_2 (or variation in quantity) was not evident. In some instances high concentrations of ClO_2 were found in highly reactive systems, but other reactive systems yielded only moderate concentrations. Conversely, systems which nominally appeared to be compatible nearly always gave a modest increase in ClO_2 content. We conclude therefore that EPR can reliably be expected to give evidence of effects not easily detected by other methods, and is perhaps more useful for this purpose than for monitoring gross or fairly rapid reactions. Chlorine dioxide is considered to be a secondary product, one which happens to be relatively stable and thus persists, rather than a first product of decomposition or reaction. We expect the concentration of ClO_2 to be highly dependent on several factors, including its own reactivity, and it is not surprising that ClO_2 concentration cannot be equated with the extent or rate of reaction in NP systems.

1. Studies of the NP system: The NP system we define as follows: NO_2ClO_4 is the predominant species. In addition, NP contains small quantities of $NOClO_4$ and products of hydrolysis of NO_2ClO_4. The hydrolysis products are nominally HNO_3 and $HClO_4$. The most accurate description of hydrolysis with a deficiency of water is probably represented by the equations

$$2H_2O + NO_2ClO_4 \longrightarrow H_3OClO_4 + HNO_3$$

$$H_3OClO_4 + NO_2ClO_4 \rightleftarrows HNO_3 + 2HClO_4$$

Two moles of water react with one of NO_2ClO_4 to generate hydronium perchlorate and one mole of essentially free nitric acid. The water of the hydronium ion participates in a reversible reaction with a second mole of NO_2ClO_4, with the equilibrium lying far to the left in the equation as written. Complicating this picture is the formation of a crystallographically unique species composed empirically of one mole each of H_3OClO_4 and NO_2ClO_4. This species volatilizes as HNO_3 + $2HClO_4$, which reform the unique crystalline phase on recondensation (Ref. 6). "Wet" NP thus may contain nitric acid at relatively high pressures, perchloric acid at a relatively low pressure, and H_3OClO_4. Hydronium perchlorate crystallizes uniquely with one mole of NO_2ClO_4, and it is reasonable to expect lattice interactions with an excess of NO_2ClO_4.

In addition to the above impurities, commercial NP undoubtedly contains small quantities of additional foreign substances. Likely impurities are metal oxides or perchlorates, and carbonaceous substances. This group of impurities were not investigated in this program. They may well be important, but as yet suitable methods for analysis and identification are not available. We have found substantial effects attributable to the water-$NOClO_4$ class of impurities. These effects are now well documented but still not understood, and investigations of these effects have been given precedence over a broader study of purity.

Initial studies of NP revealed the existence in the solid phase of the radical molecule ClO_2. Since ClO_2 is a reactant used to manufacture NP, its presence may have been due to retention of process ClO_2 rather than to post-manufacturing generation from NO_2ClO_4. Additional study showed that the concentration of ClO_2 could be increased by environmental effects. We concluded that ClO_2 was inherent in NP, and embarked on studies aimed at defining its origin and significance. The results of this investigation are summarized below (see Table 5, Figures 5 and 6).

(a) As-received (undried) NP fluff or granules contain ClO_2 at a concentration level arbitrarily set at 1-2. The approximate absolute concentration is 10^{-6} to 10^{-7} moles per mole of NO_2ClO_4.

(b) Rigorous evacuation (10^{-4} mm, ca. 3 days) reduces the ClO_2 content to a still detectable level in 3 - 4 mole samples contained in 8 mm vycor tubes. In 3 mm ID tubes ClO_2 cannot ordinarily be detected in dried NP.

(c) In no instance, including later described conditions, was ClO_2 detected in the gas phase above NP.

(d) Addition of water, at about 1 per cent by weight, to dried NP causes an increase in ClO_2 content. The level may go significantly above the as-received level, but after 2 - 3 weeks the ClO_2 level is about the same as that in as-received NP.

(e) Extended heating at 60° (up to 70 hr.) resulted in no significant increase or decrease in ClO_2. Times of the order of 30 min. at temperatures as high as 110° also caused no change. At 125°, ClO_2 in high concentration was evolved; since sealed tubes were employed, these experiments were terminated early to avoid rupture of the tube in the EPR cavity.

(f) Nitrogen dioxide absorbs on NP decomposed partially by extended heating at 60°C or by short periods at 125°C. The absorbed NO_2 is detectable by EPR after brief evacuation at 10^{-4} mm, and is desorbed only after evacuation for several hours.

(g) Addition of $NOClO_4$ (10 per cent) to NP results in a slow increase in ClO_2 content to a moderate level.

(h) Addition of $NOClO_4 + H_2O$ to NP results in a marked increase in ClO_2 content, if $NOClO_4$ is the minority constituent (<50 per cent). With 50-50 mixtures the effect is modest; $90NOClO_4$-$10NO_2ClO_4$-xH_2O and 99-1-xH_2O mixtures thus far contain no ClO_2. This trend continues as $NOClO_4$ is reduced to 10 per cent and 1 per cent. At both low proportions of $NOClO_4$ the ClO_2 contents become quite high (1500 - 3000 relative, ca. 10^{-3} molar absolute), and 1 per cent $NOClO_4$ was more effective than 10 per cent $NOClO_4$.

The quantity of added water is also a significant variable, as higher ClO_2 contents were generated with higher added quantities of water.

TABLE 5

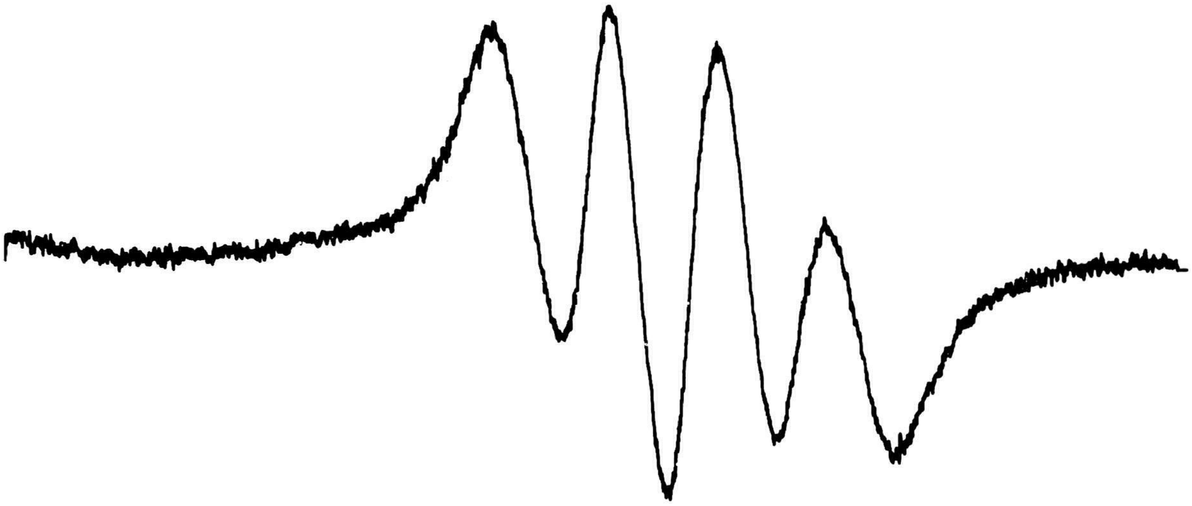
EPR STUDIES OF NP AND RELATED SYSTEMS

t = time in days
I = Relative signal intensity
Signal = ClO_2 unless otherwise stated
Number Preceding Compounds Indicate Relative Molar Proportions

System	t	I
NP, undried		1-2
NP, dried		<1
$NOClO_4$	54	<1
$I00NOClO_4-6H_2O$	54	<1
$1\ NO_2ClO_4-99NOClO_4-6H_2O$	54	<1
$10\ NO_2ClO_4-90NOClO_4-6H_2O$	54	<1
$50\ NO_2ClO_4-50NOClO_4$	54	<1
$50\ NO_2ClO_4-50NOClO_4-2H_2O$	51	<1
$50\ NO_2ClO_4-50NOClO_4-6H_2O$	5	30
	13	12
	20	190
	36	25
	41	100
	54	25
$50\ NO_2ClO_4-50NOClO_4-20H_2O$	5	180
	13	10
	20	10
	36	1
	41	10
	54	1
$90\ NO_2ClO_4-10NOClO_4-13H_2O$	5	1200
	14	1400
	42	140
	56	500
	70	160
	83	500

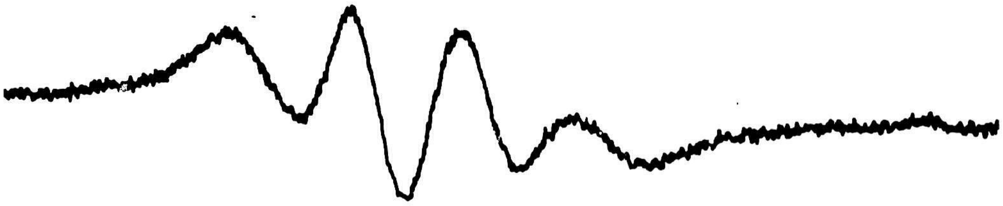
TABLE 5 (Concluded)

System	t	I
90 NO_2ClO_4-10$NOClO_4$-13H_2O (concluded)	120	1200
	138	800
	172	420
90NO_2ClO_4-10$NOCl_4$	5	70
	15	70
	42	20
	172	8
99NO_2ClO_4-1$NOClO_4$-6H_2O	5	1400
	13	1000
	20	2600
	36	1000
	54	800
100NO_2ClO_4-10H_2O	1	7
	14	35
	20	7
NO_2ClO_4-HNO_3(20 mm)	1	2
	57	4
50NO_2ClO_4-50$NOClO_4$-HNO_3 (20 mm)	0	<1
	6	45
	29	170
	47	220
NO_2ClO_4-HNO_3 (20 mm)	20	2
$NOClO_4$-HNO_3 (20 mm)	0	<1
	13	1
	29	20 (NO?)
	47	300 (NO?)
$HClO_4$(l)	0	1
	1	5
1NO_2ClO_4-1H_3OClO_4	14	1
	34	2
XS NO_2ClO_4-H_3OClO_4	1	4
	7	8
	20	3
NO_2ClO_4-oleum	2	55
	23	30



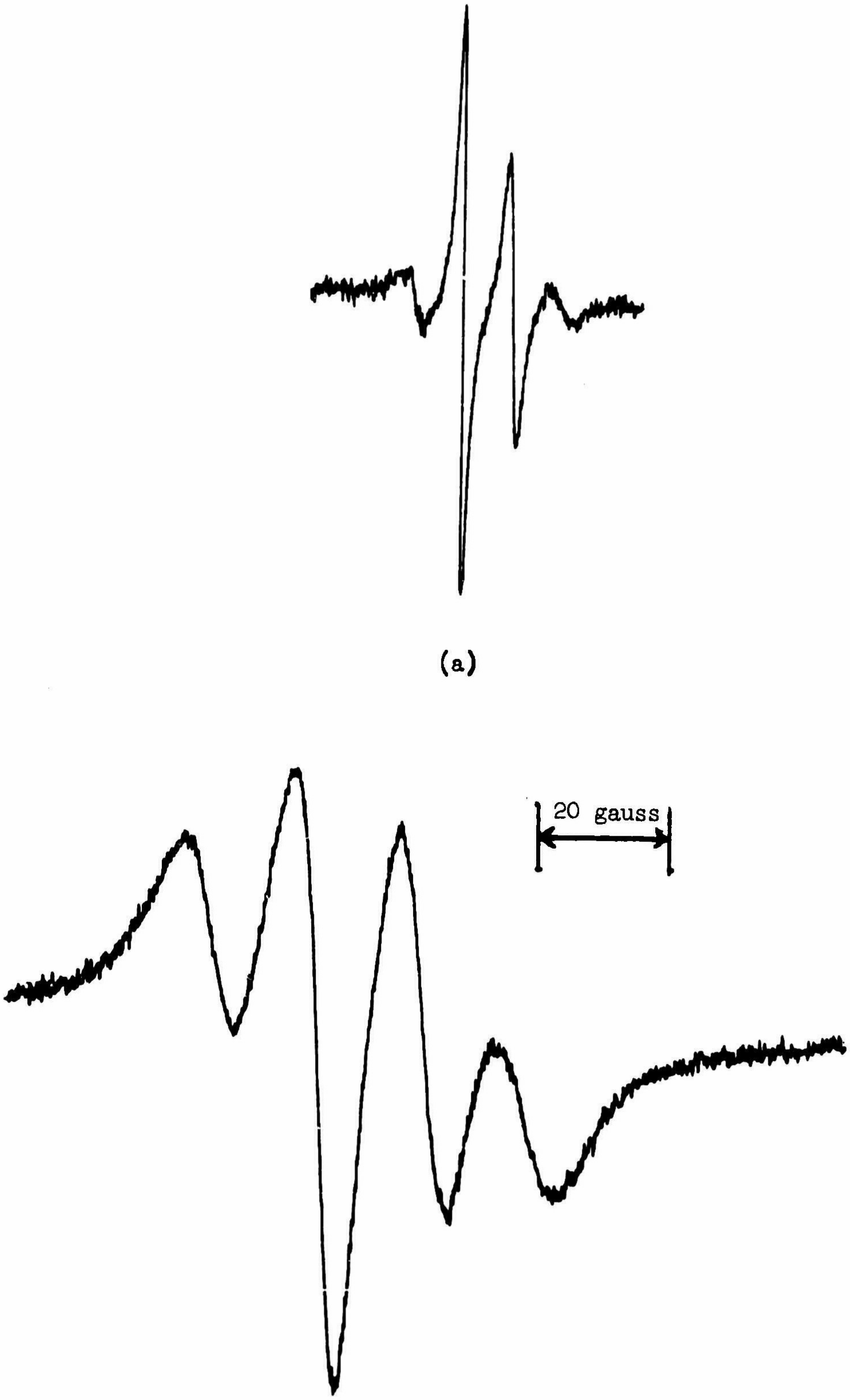
Undried
Fluff

Evacuated 80 Hr.



Evacuated 24 Hr.

Figure 5 - EPR Spectra of ClO_2 in NP



(a)

(b)

Figure 6 - EPR Spectra: (a) ClO; (b) ClO_2

(i) $NOClO_4$-NO_2ClO_4-H_2O mixtures which generate high concentrations of ClO_2 proceed through cycles of low and high ClO_2 content.

(j) $NOClO_4$ by itself has never yielded detectable quantities of ClO_2, in spite of the fact that dry $NOClO_4$ without exception has visibly (brown gases) decomposed after storage for about one month at ambient temperatures. The evolution of NO_2 has occurred in sealed EPR tubes and in evacuated storage vessels stoppered with lubricated ground joints. To the best of our knowledge $NOClO_4$ has not previously been observed to be unstable at ambient conditions.

(k) $NOClO_4$ plus water does not result in ClO_2 generation. Significantly, visible evidence (brown gases) of decomposition does not appear with wet $NOClO_4$. We do not have confirming evidence, but nevertheless we are of the opinion that added water removes visual evidence of decomposition by reacting with NO_2, and that water does not stabilize $NOClO_4$.

Exposure of $NOClO_4$ to gaseous nitric acid results in the slow development of an EPR signal which we tentatively attribute to nitric oxide.

(l) ClO_2 was generated in modest concentration when the following substances were added to dry NP: gaseous nitric acid, H_3OClO_4, and sulfuric acid (120 per cent SO_3).

(m) Anhydrous perchloric acid produced ClO_2 within one day; the dielectric loss was thereafter so high that the sample could not be tuned in the cavity. A small sample of H_3OClO_4-NO_2ClO_4 was sublimed into an EPR tube; after several days the sample contained ClO_2.

(n) Addition of varied organic substances to NP invariably (except methane) resulted in ClO_2 generation (see Table 6). This subject will be discussed in greater detail in the following subsection.

It is obvious that substances inherent in NP ($NOClO_4$; water as HNO_3, $HClO_4$ and H_3OClO_4) promote the formation of ClO_2, and that certain of these ($HClO_4$, H_3OClO_4) are by themselves sources of ClO_2. Within the limits of the study, it is obvious that ClO_2 is to be expected if NP is contacted with any but the most inert materials. Finally, it is clear that certain combinations of NP, $NOClO_4$, and water are uniquely capable of generating high concentrations of ClO_2.

Can one conclude that NO_2ClO_4, the pure material, is unstable at ambient conditions? The data do not provide the answer to this question. The NP used in the investigations undoubtedly contains impurities which have been shown to be sources of ClO_2 or promoters of phenomena which yield ClO_2. It is

TABLE 6

EPR STUDIES: NP PLUS ORGANIC MATERIALS

t = time in days
I = relative signal intensity (dry NP 1)
Signal = ClO_2 unless otherwise stated

Added Substance	t	I
MRPX-UTREZ-NTEB	2	<1
	42	300
	76	5
MRPX	6	1
	26	100 (ClO)
	47	<1
MRPX-undried NP	3	2
	12	20 (ClO)
	26	200 (ClO)
	40	<1
NTEB in CCl_4	2	5
	22	80
	85	80
HMT in CCl_4	7	30
	21	1800
	55	240
CHP in CCl_4	0	700
	5	4000
Hexane (gas)	4	60
	7	350
	18	400
	41	550
	59	550
Neopentane (gas)	1	10
	6	30
	20	40

TABLE 6 (Concluded)

Added Substance	t	I
Propane (fractionated gas)	2	10
	5	50
	42	50
Propane (unfractionated gas)	5	400
CH_3Cl	2	15
	14	60
	42	20
C_2H_6	1	10
	34	10
CH_4	20	<1

our opinion that the NP-containing sample freest of unknown impurities was sublimed H_3OClO_4-NO_2ClO_4. The observation of ClO_2 in this sample indicates that $NOClO_4$ is not necessary for ClO_2 generation. The sample was of course far from being pure NO_2ClO_4.

The next pertinent question is this: Does ClO_2 come directly from the NO_2^+, ClO_4^- ion pair, or is perchloric acid, hydronium perchlorate or $NOClO_4$ the immediate source of ClO_2? This question we also cannot answer with certainty. It is true that some ClO_2 persists in well dried NP, but one cannot say with certainty that the NP was completely dry, or that residual $NOClO_4$ did not promote ClO_2 formation.

One thus must for the present be satisfied with the conclusion that NP as it presently is known and available inherently contains ClO_2 in concentrations normally considered to be trace, and that certain treatments can increase this concentration very substantially. This conclusion leads in our opinion to a second conclusion, namely that NP the practial material is fundamentally unstable at ambient conditions, even though this instability is not evidenced by rates of decomposition of practical significance. This conclusion may be restated as follows: The elements of instability persist in NP at ambient conditions, but they are manifested by quantities of decomposition products small enough to escape detection save in the most careful and time-consuming studies. One concludes further that the inherent stability of NP in a reactive environment will diminish as reaction produces nitric acid, perchloric acid, and possibly $NOClO_4$. In other words, products of NP-fuel reaction will promote the autodecomposition of NP.

2. The mechanism of ClO_2 formation: In earlier reports (Refs. 10 and 11), the chemistry of NO_2ClO_4, $NOClO_4$, NO_2, HNO_3, $HClO_4$ and other pertinent species were discussed in attempts to pinpoint the means by which ClO_2 is generated. The arguments disintegrated when it was discovered that ClO_2 is not present in wet or dry $NOClO_4$. The fact framework is now firmer, and additional interpretative rationale has been suggested.

Pertinent facts are: (1) $NOClO_4$ and $HClO_4$ (or H_3OClO_4) are present in NP; both are formally capable of ClO_2 formation; ClO_2 has been detected in $HClO_4$, not in $NOClO_4$; (2) $NOClO_4$ is unstable, must certainly yield chlorine and chlorine oxides, but the chlorine oxides are evidently unstable over or in $NOClO_4$; (3) ClO_2 obtains readily in NP-$NOClO_4$-H_2O containing small proportions of $NOClO_4$, and not at all in the same system containing small proportions of NP. It thus appears that $NOClO_4$ promotes ClO_2 in NO_2ClO_4, rather than vice versa; (4) paramagnetic NO_x radical molecules are not detected by EPR unless decomposition has proceeded to the point of visual NO_2 generation; and (5) the additives H_2O + $NOClO_4$ are uniquely effective.

Since NP may never be completely dry or free of $NOClO_4$, one can argue that even the small quantities of ClO_2 seen in "dry" NP are due to the presence of water and $NOClO_4$, with an assist from NO_2ClO_4 as a provider of $HClO_4$. In line with this thinking the following mechanisms can be proposed.

(a) $NOClO_4$ as prime source of ClO_2

$$NO^+ClO_4^- \rightleftharpoons NO_2^+,\ ClO_3^- \rightleftharpoons NO_2 + ClO_3$$

$$ClO_3 \longrightarrow ClO_2 + \tfrac{1}{2}O_2$$

$$\text{or } ClO_3 + NO^+ \longrightarrow NO_2^+ + ClO_2$$

$$2NO_2 + H_3OClO_4 \longrightarrow NOClO_4 + HNO_3 + H_2O$$

$$2H_2O + NO_2ClO_4 \longrightarrow H_3OClO_4 + HNO_3$$

$$ClO_2 \longrightarrow \cdot ClO \longrightarrow Cl_2$$

These reactions may be summed in several ways. The simplest is:

$$2NOClO_4 + H_2O \longrightarrow 2HNO_3 + 2ClO_2 + \tfrac{1}{2}O_2$$

To complete the process, ClO_2 decomposes so that nitric acid, chlorine, and oxygen are the ultimate products.

The essential features of the above mechanism are a reversible formation of NO_x and ClO_x radical molecules (NO_2 and ClO_3 are likely possibilities), and a removal of NO_2 from the equilibrium by reaction with $HClO_4$. The primary ClO_x radical then has no recourse but to decompose or react with available species, and ClO_2 is the relatively stable result. It is suggested that the NO^+ ion can be readily oxidized to NO_2^+. The absence of ClO_2 in $NOClO_4$ or in NP-$NOClO_4$ mixtures high in $NOClO_4$ is logically accounted for in this basis.

$$NO^+ + ClO_2 \longrightarrow NO_2^+ + ClO$$

(b) Anhydrous perchloric acid is noted for its tendency to decompose, yielding hydronium perchlorate, chlorine oxides, chlorine and oxygen. This tendency is evidently slight in the equilibrium quantities of free perchloric acid present in slightly wet NP. A mechanism involving $HClO_4$ as the prime source of ClO_2 must therefore include a means to shift an equilibrium or provide a new route for decomposition. The NO^+ ion may well serve this purpose, possibly by being oxidized to the NO_2^+ ion or to HNO_3 and thus serving as a scavenger of oxygen. We prefer not to suggest a detailed mechanism -- one quickly becomes embroiled in sets of equations which lead by devious routes to HNO_3, ClO_2 and O_2, and the preferred route is not obvious.

With either approach to a mechanism, $NOClO_4$ and $HClO_4$ are the prime movers, and NO_2ClO_4 is a relatively innocent bystander. This interpretation could be construed as evidence that NO_2ClO_4 in the pure state would be significantly more stable than the available, not quite pure state. While this question is presently unanswered, it is well known that certain impurities enhance stability, and that sublimed NP decomposes more readily than the unsublimed material. Water, or H_3OClO_4, is in fact a desirable impurity from the standpoint of stability at temperatures of the order of 60 - 70°C. The enchanced stability with added water can be reconciled with the observation in this program that water decreases stability as measured by ClO_2 generation, if one assumes that water converts NO_2 to HNO_3. Vigorous decomposition occurs only after NO_2 has been generated in measurable quantities, and it is commonly believed that NO_2 catalyzes or promotes the decomposition of NP. The role of water is thus conversion of NO_2 to relatively innocuous species.

We subscribe to the thesis that NO_2ClO_4 even at ambient temperatures has some covalent character, as substantiated by X-ray (Ref. 12), vibration spectra (Ref. 13), and its ability to sublime. Anion and cation interact to a degree sufficient to effect distortions of bond angles and distances. If the ions interact to this extent, one should not be surprised if a small fraction interact further, by charge transfer, by formation of molecular NO_2ClO_4, or by transfer of charge and oxygen atoms.

$$NO_2^+, ClO_4^- \rightleftharpoons NO_2 + ClO_4$$

$$NO_2^+, ClO_4^- \rightleftharpoons NO_2ClO_4^*$$

$$NO_2^+, ClO_4^- \rightleftharpoons NO_3 + ClO_3$$

Loss of oxygen atoms from any of these states should result in formation of $NOClO_4$.

$$NO_2^+, ClO_4^- \rightleftharpoons NO_2 + ClO_4$$

$$ClO_4 \longrightarrow ClO_3 + O$$

$$NO_2 + ClO_3 \longrightarrow NOClO_4$$

Additional loss of oxygen would yield ClO_2. This rationale leads to the conclusion that pure NO_2ClO_4 should contain trace quantities of chlorine oxides and nitrogen oxides, and should as a consequence be less stable than slightly impure, or slightly wet NP. The rationale is presented also to support a conviction that NO_2ClO_4 is more than passively involved in ClO_2 generation. This conviction has not been verified by our results, but it has not been disproved.

The slow cycling of ClO_2 concentration in certain NP-$NOClO_4$-H_2O samples can be qualitatively explained. Calculated pressures of ClO_2 at maxima are of the order of 40 - 50 mm. The ClO_2 is trapped in interstices of crystal lattices or strongly adsorbed on crystal surfaces. Chlorine dioxide is stable in the gas phase only at low pressures. It is thus possible that effective pressures become too high in localized sites, and decomposition ensues. Alternatively, ClO_2 generation may best occur at localized sites in which conditions (availability of $HClO_4$, $NOClO_4$, etc.) are ideal. As ClO_2 forming reactions occur at these sites, conditions depart from ideality, and rates of decomposition surpass rates of formation. Regeneration of ideal conditions can be effected by a mechanism such as transfer of $HClO_4$ through the gas phase, and the cycle then repeats. This cycling mechanism likely would involve movement of reactive sites through crystal phases.

Comments are in order about systems not specifically covered in the above discussion of mechanisms.

Nitric acid added to NP yields a small increase in ClO_2. We suggest no firm mechanism, but wish to point out that nitric acid can be expected to participate in reactions such as:

$$HONO_2 + N'O_2 \longrightarrow HON'O_2 + NO_2^+$$

an exchange reaction accompanied by momentary disarrangement in lattices at surfaces, and

$$HONO_2 + NO_2ClO_4 \rightleftarrows HClO_4 + N_2O_5,$$

an equilibrium far to the left, but significant enough to generate species unstable with respect to loss of oxygen.

Gaseous nitric acid and $NOClO_4$ yield an unidentified radical or radical molecule which may be NO. Since the identity of the radical is not known for certain, speculation about mechanisms are somewhat pointless. A second curious feature of the nitric acid - $NOClO_4$ sample is the absence of brown gases. Untreated $NOClO_4$ samples prepared at the same time have evolved NO_2.

The explanation of ClO_2 in H_2SO_4-NP is simple. Sulfuric acid reacts as follows with NO_2ClO_4:

$$H_2SO_4 + NO_2ClO_4 \longrightarrow NO_2HSO_4 + HClO_4$$

Free perchloric acid is the obvious source of ClO_2.

With reactive organic materials and NP one is at liberty to choose between three general types of mechanisms: (1) generation, by reaction, of HNO_3, $HClO_4$, and $NOClO_4$, which then interact with one another and with NP; (2) formation of organoperchlorates which yield ClO_2 on decomposition; and (3) oxidation reactions which strip oxygen from the ClO_4 group.

With nominally non-reactive organic substances and NP the important question is whether ClO_2 generation results from organic-NP reaction. Other possibilities are reaction with trace constituents, inadvertent introduction of water, purely physical effects such as strong absorption of molecules on NP, or combinations of these. We cannot, with present data, resolve this question.

3. Chlorine dioxide in organic - NP systems: As mentioned before, ClO_2 appeared in all these systems save in NP-CH_4. The behavior can generally be described as follows.

(a) Systems which reacted without question, as measured by infrared, generated ClO_2 in moderate to high concentrations (100 to 4000 times that of undried NP). NP-MRPX, NP-hexane, NP-CCl_4-NTEB, NP-CCl_4-CHP and NP-MRPX-UTREZ-NTEB are included in this group.

(b) Systems which reacted more slowly, or for which infrared evidence indicated change not positively attributable to reaction, generated from 10 to 100 times the ClO_2 found in undried NP. These systems are NP-ethane, NP-propane, NP-neopentane, and NP-methyl chloride.

(c) With the more reactive systems, ClO_2 concentrations often decreased to a low level (1 to 10) after reaching a maximum. The decrease we feel means that the environment created by fairly gross reactions is incompatible with ClO_2.

(d) Chlorine monoxide supplanted ClO_2 as the major radical in NP-MRPX after about two weeks, and persisted for 4 - 5 additional weeks.

(e) The signals generated in nominally non-reactive systems (i.e., NP-ethane) persisted without appreciable change for several weeks. This behavior would be expected of a system which reacts slowly but steadily.

These observations need little amplification. High reactivity is more or less synonymous with high ClO_2 contents, but ClO_2 is not a reliable measure of differences in reactivity in reactive systems. For example, undried NP-MRPX and dry NP-MRPX differed little by EPR, and very significantly by infrared.

Of significance is the fact that even the most compatible hydrocarbons (neopentane, ethane and propane) yielded ClO_2 in higher than normal levels. As discussed previously, several explanations can be given. With all of the explanations, one concludes that NP-hydrocarbon contact has resulted in evidence of instability or reactivity. The induced instability or reactivity may be small. It has occurred in high purity systems under ideal conditions, however, and one should not be surprised if non-laboratory conditions and lower purity (or less specific structures) materials result in substantially increased reactivity.

III. SUMMARY AND CONCLUSIONS

The results of this program may be summarized as follows.

1. The compatibility of NP with the binder system evaluated in this program is not adequate at ambient temperatures (75 - 78°C). At 42°F reaction rates are lowered considerably, but are not eliminated.

2. Tests of simple liquid hydrocarbons showed them to be slowly reactive with NP.

3. Simple gaseous hydrocarbons yielded ambiguous evidence which may indicate slow reaction with NP.

4. In two aged Reta coated NP samples, evidence of reaction and of failure of the protective polymer was found.

5. NP itself exhibits evidence (ClO_2) of inherent instability at ambient temperatures.

6. NP should in practical operations be viewed as a substance containing volatile nitric acid and perchloric acids. The presence of these acids imparts to NO_2ClO_4 the ability to volatilize.

Conclusions which may be drawn are several. These are adequately summed up in two statements.

1. Of the materials tested, only the simplest and purest of hydrocarbons were sufficiently non-reactive to be suitable for long-term contact with NP, and the achieving of adequate compatibility in a practical binder system thus poses a very formidable, though not necessarily impossible, task.

2. Inherent properties of NP other than its recognized reactivity contribute to the compatibility picture. These inherent properties impose the requirement that an organic phase in direct contact with NP must be at least as inert as binders are to AP, if lasting compatibility is to be realized.

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13. ABSTRACT

The compatibility of nitronium perchlorate with various organic materials, including a solid propellant binder system, has been investigated. Infrared and electron paramagnetic resonance spectroscopy were employed to measure reactivity.

The results indicate compatibility between raw NP and the system to be less than satisfactory. Studies of simple hydrocarbons gave the following results. Hexane, n-pentane and isooctane react slowly with NP, at ambient temperatures; HNO_3, NO_2Cl, N_2O and CO_2 are major reaction products. Methane does not appear to react. Ethane, propane and neopentane are not detectively consumed by NP, but nitric acid is generated in small quantities along with perchloric acid. It has been tentatively concluded that the latter substances react very slowly with NP.

Chlorine dioxide is inherently present at low concentrations in dry, commercial NP. Concentrations are slightly higher in undried NP. Addition of NP to water, $NOClO_4$, HNO_3, H_3OClO_4, and all tested organic substances except methane resulted in increased ClO_2 concentrations. Two samples of Reta-coated NP contained higher than normal concentrations of ClO_2. One concludes generally that NP is slightly unstable at ambient temperatures, that substances inherent in NP enhance the instability, and that added foreign substances promote ClO_2 formation. The formation of ClO_2 can be used as a qualitative measure of the reactivity of organic materials.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
NO_2ClO_4						
NP						
Advanced oxidizers						
Perchlorates						
Stability						
Compatibility						
Reaction chemistry						
Solid propellants						
Nitric acid						
Perchloric acid						
Infrared spectroscopy						
Electron Paramagnetic Resonance Spectroscopy						
Free radicals						
Chlorine oxides						
Nitrogen oxides						