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INVESTIGATION OF THE MECHANISM OF THE UNIMOLECULAR AND THE ELEC--ETC(U)
JAN 79 G B SCHUSTER, B G DIXON N00014-76-C-0745
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The mechanism of the thermolysis of 1-phenylethyl peroxyacetate was studied. In the absence of easily oxidized substrates this perester undergoes thermal fragmentation to yield quantitatively acetophenone and acetic acid. These products are formed by initial oxygen-oxygen bond homolysis followed by in cage hydrogen atom transfer. A small fraction of the so formed acetophenone is generated in an electronically excited state. In the presence of easily oxidized substrates the reaction of the perester is catalyzed and generates excited states by the chemically initiated electron-exchange lumi-

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by

(10) Gary B. Schuster [redacted] Brian G. Dixon

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Investigation of the Mechanism of the Unimolecular and The Electron Donor Catalyzed Thermal Fragmentation of Secondary Peroxy Esters. Chemiluminescence of 1-Phenylethyl Peroxyacetate.

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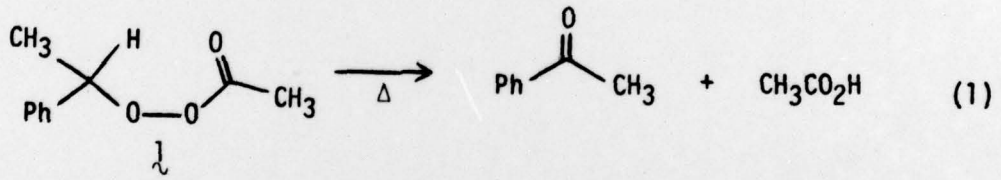
Abstract:

The mechanism of the thermolysis of 1-phenylethyl peroxyacetate was studied. In the absence of easily oxidized substrates this perester undergoes thermal fragmentation to yield quantitatively acetophenone and acetic acid. These products are formed by initial oxygen-oxygen bond homolysis followed by in cage hydrogen atom transfer. A small fraction of the so formed acetophenone is generated in an electronically excited state. In the presence of easily oxidized substrates the reaction of the perester is catalyzed and generates excited states by the chemically initiated electron-exchange luminescence (CIEEL) mechanism. An analogy with the catalyzed reaction is drawn to the excitation step of bacterio-luminescence.

Investigation of the Mechanism of the Unimolecular and the Electron Donor Catalyzed Thermal Fragmentation of Secondary Peroxy Esters. Chemiluminescence of 1-Phenylethyl Peroxyacetate.

Sir:

Our interest in highly exoergic thermal reactions of organic peroxides led us to the investigation of 1-phenylethyl peroxyacetate (1). Thermolysis of 1 in benzene solution gives a quantitative yield of acetic acid and acetophenone,[1] a small fraction of which is electronically excited. The reaction of 1 is catalyzed by a wide range of easily oxidized substances. In this case, the electronically excited state of the catalyst (activator) is formed, apparently by the recently described chemically initiated electron-exchange (CIEEL) mechanism.[2] We report herein our examination of the mechanism of both the unimolecular and catalyzed reaction of 1.



(1)

Perester 1 was prepared by the acid catalyzed reaction of ketene with 1-phenylethylhydroperoxide in CH_2Cl_2 and purified by distillation.[3] The thermolysis of 1 in argon purged benzene can be followed conveniently by the indirect or activated[4] chemiluminescence that results upon addition of biacetyl or any one of several easily oxidized fluorophores (see below) respectively. The rate at which the perester reacted showed apparent first-order kinetic behavior. However, the observed rate constants and derived activation parameters for solutions 1×10^{-2} M and above are dependent upon the initial perester concentration, indicating the likely involvement of a radical induced homolysis path.[5] At low

initial perester concentration (1×10^{-5} - 1×10^{-3} M) the rate of reaction is independent of concentration. Moreover, the activation parameters for the reaction, $\Delta H^{\ddagger}$ = 33.2 ± 0.7 kcal/mole, $\Delta S^{\ddagger}$ = 11.0 ± 1.9 eu (see Figure 1), under these conditions indicate a unimolecular process.[6]

In contrast to the modified Russell mechanism[7] suggested by Hiatt and co-workers[8] for the thermolysis of secondary peresters, our findings are more consistent with a stepwise process in which oxygen-oxygen bond homolysis is followed by rapid in-cage hydrogen atom abstraction. In particular, the activation enthalpy indicates a transition state in which bond cleavage is uncompensated by bond formation.[6] And the quantitative yield of acetic acid rules out escape from the solvent cage of a significant amount of the so formed acetyloxy radical.[9] The calculated heat of reaction for the process shown in eq. 1 is -58 kcal/mole.[10] Thus, the transition state for this reaction lies some 94 kcal/mole above ground state products. Sufficient energy is released therefore to populate electronically excited states of acetophenone.[11] Indeed, we detect a low yield of excited state product as indirect chemiluminescence from added biacetyl. The emission spectrum of the chemiexcited biacetyl is composed entirely of the phosphorescence, thus implicating acetophenone triplet as its precursor. This mechanism is shown as path A in Scheme I.

When a small amount of an easily oxidized substance is added to benzene solutions of perester 1, the thermolysis reaction is somewhat different. For example, N,N-dimethyldihydrodibenzo[a.c]phenazine (DMAC)[12] accelerates the rate of reaction of 1 (Figure 2) without itself being consumed. The products of this reaction are acetic acid and acetophenone, formed quantitatively as they were for the uncatalyzed case. Electronically excited states are formed by the catalytic reaction as well, and, in contrast to the unimolecular transformation, are detected as the

fluorescence of the excited singlet state of the activator. The DMAC is not unique in its catalytic ability. Similar observations were made for N,N-diphenyl-2-aminopyrene (DPAP),[13] zinc tetraphenylporphyrin, rubrene, perylene, 9,10-diphenylethynylanthracene, and others.

The relative catalytic rate constant for the various activators was determined by measuring the total chemiluminescent light intensity under conditions where most of 1 reacted by the unimolecular path (i.e low activator concentration). After correcting for differences in fluorescence quantum yield and photomultiplier tube and monochromator spectral efficiency, it is apparent that the only correlation of activator property and rate constant is with the one electron oxidation potential (Table 1 and Figure 3).

These findings are just those that one would expect for a CIEEL process. Electron transfer from the activator to perester 1 is endothermic but may be made irreversible by rapid cleavage of the oxygen-oxygen bond of the reduced peroxide. The rate of this reaction is expected to depend upon the oxidation potential of the activator. Transfer of a hydrogen atom simultaneously with or subsequent to oxygen-oxygen bond cleavage generates acetophenone radical anion in the same solvent cage as the activator radical cation. Charge annihilation of these radical ion intermediates leads to the observed excited state product. This mechanism is shown as path B in Scheme I for DMAC.

This is the fourth well-documented case of an electron-transfer initiated reaction of a peroxide that leads to electronically excited state product.[2] As in the previously described examples, the major evidence is the correlation of rate constant and oxidation potential, i.e. Figure 3. Comparisons among the various peroxides reveal that the catalytic rate constant is strongly dependent upon structure--diacylperoxides react much more rapidly than

peresters, which are more difficulty reduced, for example.[14] However, the magnitude of the slope of the line resulting from the semilog plot of rate against activator oxidation potential is essentially constant and equal to ca. -0.3/RT for the systems investigated to date. This result is consistent with rate limiting irreversible electron transfer from activator to peroxide occurring with a trasfer coefficient of ca. 0.3.[15]

In summary, we have observed two distinct reaction paths for thermolysis of secondary perester 1. The unimolecular reaction appears to proceed by a step-wise route, the bimolecular reaction with electron donors by an electron transfer mechanism. The electron transfer mechanism in particular may serve as a model for the excitation step in the bacterioluminescence reaction.[16] We are continuing our investigation of this and other aspects of the chemistry of these peresters.

Acknowledgment. We would like to thank Professor Faulkner of this department for many helpful discussions. The authors gratefully acknowledge financial support for this work by the Office of Naval Research, The National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We would also like to thank Mr. Steven P. Schmidt for preparing and purifying the DMAC and DPAP.

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References and Notes

1) The products were identified by comparison with authentic material. The yield of acetic acid was determined by gas chromatography on a Poropak Q column at 245°C; the yield of acetophenone by gas chromatography on a 3% SE-30 on Chromasorb Q column at 100°C.

2) J.-y. Koo and G. B. Schuster, J. Am. Chem. Soc., 100, 4496 (1978); S. P. Schmidt and G. B. Schuster, ibid., 100, 1966 (1978); J. P. Smith and G. B. Schuster, ibid., 100, 2564 (1978); J.-y. Koo and G. B. Schuster, ibid., 99, 6107 (1977).

3) Peroxy ester 1 was characterized as follows: IR(CCl_4) 3000, 1785, 1500, 1285 cm^{-1}. ^{1}Hnmr (CCl_4 internal TMS) δ 1.50(d, 3H, J = 7 Hz), δ 1.9 (S, 3H), δ 5.17 (q, 1H, J = 7 Hz), δ 7.3 (S, 5H) Analysis: Calcd. for $C_{10}H_{12}O_3$; C, 66.64; H, 6.73; Found; C, 66.98; H, 6.66. In addition perester 1 was reduced with triethyl phosphite to 1-phenyl ethyl acetate which was characterized by comparison with authentic material.

4) We propose the following definitions:

   i) Direct chemiluminescence - The emission of light is from the excited state formed as a direct result of a unimolecular thermal chemical reaction.

   ii) Indirect chemiluminescence - The emission of light is from an excited state formed as a result of energy transfer from the initially generated excited state.

   iii) Activated chemiluminescence - The emission of light is from an excited state directly formed from a bimolecular reaction between substrate and catalyst.

5) R. A. Wolf, M. J. Migliore, P. H. Fuery, P. R. Gagnier, I. C. Sabeta, and R. J. Trocino, J. Am. Chem. Soc., 100, 7967 (1978); K. Nozaki and P. D. Bartlett, J. Am. Chem. Soc., 68, 1686 (1946).

6) W. A. Pryor and K. Smith, Int. J. Chem. Kinet., 3, 387 (1971); P. D. Bartlett and R. R. Hiatt, J. Am. Chem. Soc., 80, 1398 (1958); J. P. Lorand and P. D. Bartlett, ibid., 88, 3294 (1966).

7) G. A. Russell, J. Am. Chem. Soc., 79, 3871 (1957).

8) R. R. Hiatt, L. C. Glover, and H. S. Mosher, J. Am. Chem. Soc., 97, 1556 (1975).

9) J. C. Martin, J. W. Taylor, and E. H. Drew, J. Am. Chem. Soc., 89, 129 (1967) and references cited therein.

10) S. Benson, "Thermochemical Kinetics", 2nd Ed., Wiley, New York, NY, 1976.

11) E. B. Wilson, J. Am. Chem. Soc., 98, 3387 (1976); E. Lissi, ibid., 98, 3386 (1976).

12) J. G. Smith and E. M. Levi, J. Organomet. Chem., 36, 215 (1972).

13) Prepared by reaction of 1-aminopyrene with bromo benzene and lithium tetramethyl piperidide in THF. Analysis: Calcd. for $C_{28}H_{19}N$; C, 91.02; H, 5.18; N, 3.79; Found; C, 90.77; H, 4.99; N, 3.78.

14) For the series diphenoyl peroxide, dimethyldioxetanone, perester 1 we estimate that k_{cat} for DMAC is ca. 7×10^3, 240, 0.1 $M^{-1}s^{-1}$, respectively.

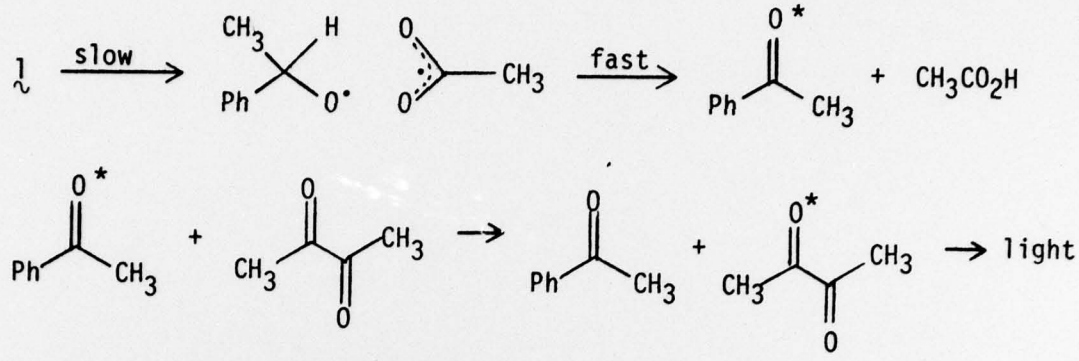
15) P. Delahay, "Double Layer and Electrode Kinetics", Wiley-Interscience, New York, NY, 1965, chapter 7.

16) J. W. Hastings and K. H. Nealson, Ann. Rev. Microbiol., 31, 549 (1977).

17) Fellow of the Alfred P. Sloan Foundation, 1977-79.

Scheme I

Path A - Indirect Chemiluminescence



Path B - Activated Chemiluminescence.

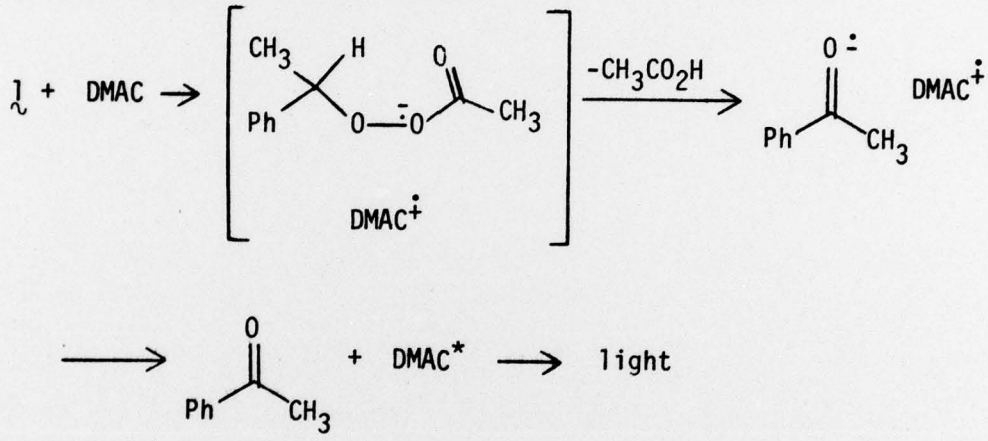


Table 1.

Activator	E_s^a (kcal/mole)	E_{ox}^b (V vs. SCE)	ϕ_{fl}^c	k_{cat}^d ($M^{-1}s^{-1}$)
Perylene	65	1.00	0.84	1.19×10^{-4}
Rubrene	54	0.82	0.56	1.40×10^{-4}[e]
Diphenylethynyl-anthracene	62	1.16	0.96	3.58×10^{-5}
DPAP	68	0.90	1.00	2.35×10^{-4}
DMAC	58	0.25	0.04	9.73×10^{-2}

a. Assigned from the 0-0 band of the fluorescence spectrum.

b. Determined by cyclic voltometry in CH_3CN solution with tetrabutyl-ammonium perchlorate supporting electrolyte.

c. At 90° in argon saturated benzene solution.

d. Calculated by comparing relative total intensity to that of DMAC.

e. Self absorption by rubrene may lead to the observed low calculated value for k_{cat}.

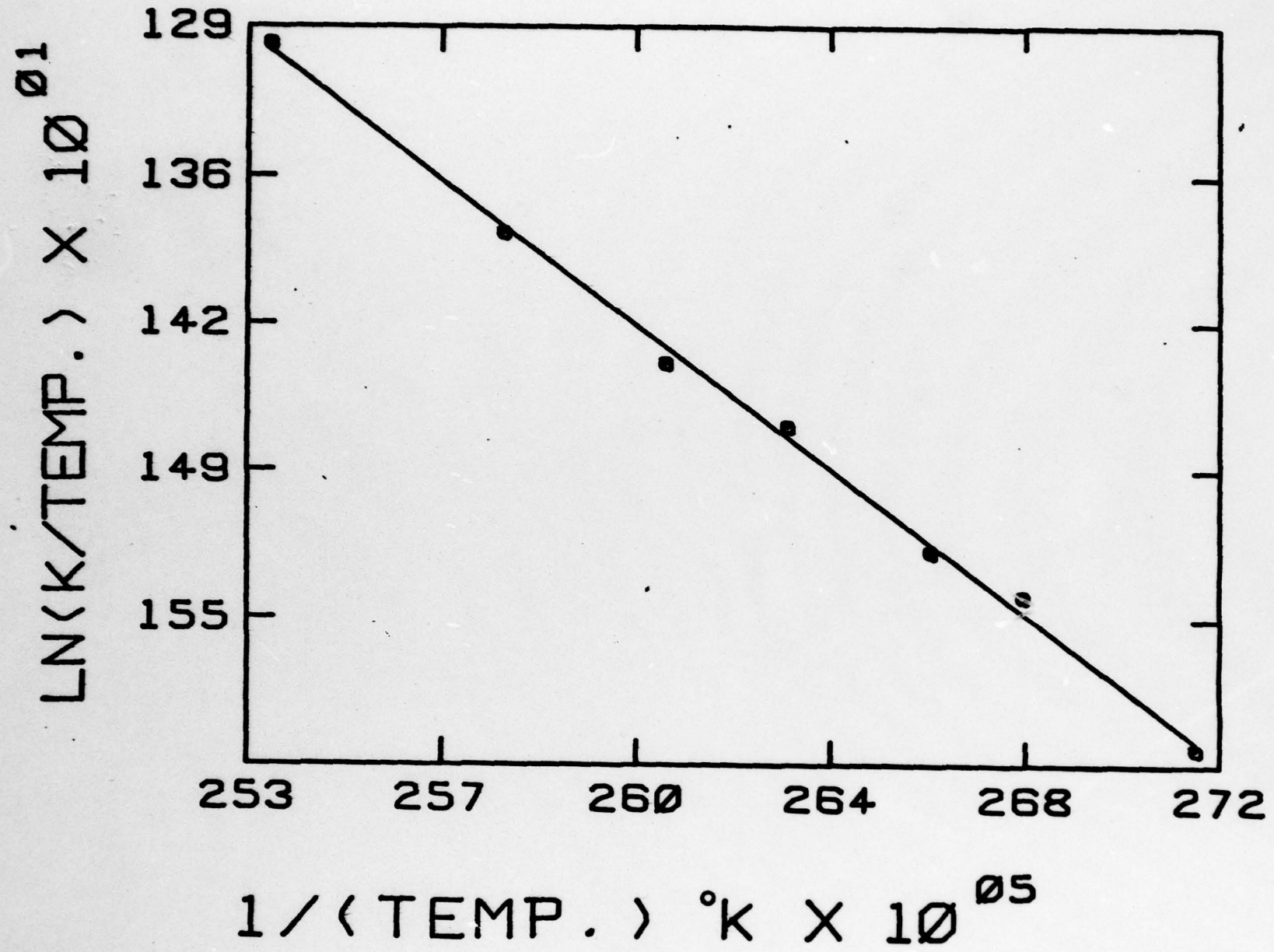
Captions for figures

Figure 1. Eyring plot for the unimolecular thermolysis of perester 1 in argon saturated benzene. Perester concentration 3×10^{-4} M. Rate constants were determined by measuring the decrease in 9,10-diphenylanthracene chemiluminescence intenstity which was shown to be directly proportional to the concentration of the perester.

Figure 2. Catalysis of perester 1 by DMAC. The observed rate constants were determined by monitoring the DMAC activated chemiluminescence in argon purged benzene solution at 99.9° and were first order for three or more half-lives. The perester was 3×10^{-4} M.

Figure 3. Correlation of total chemiluminescence intensity with activator oxidation potential (E_{ox}). The points, in order of increasing E_{ox} are: DMAC, DPAP, perylene and diphenylethynylanthracene. Measured in argon purged benzene with activator at 1×10^{-4} M and perester at 1×10^{-3} M at 99.5°.

Figure 1.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142
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155
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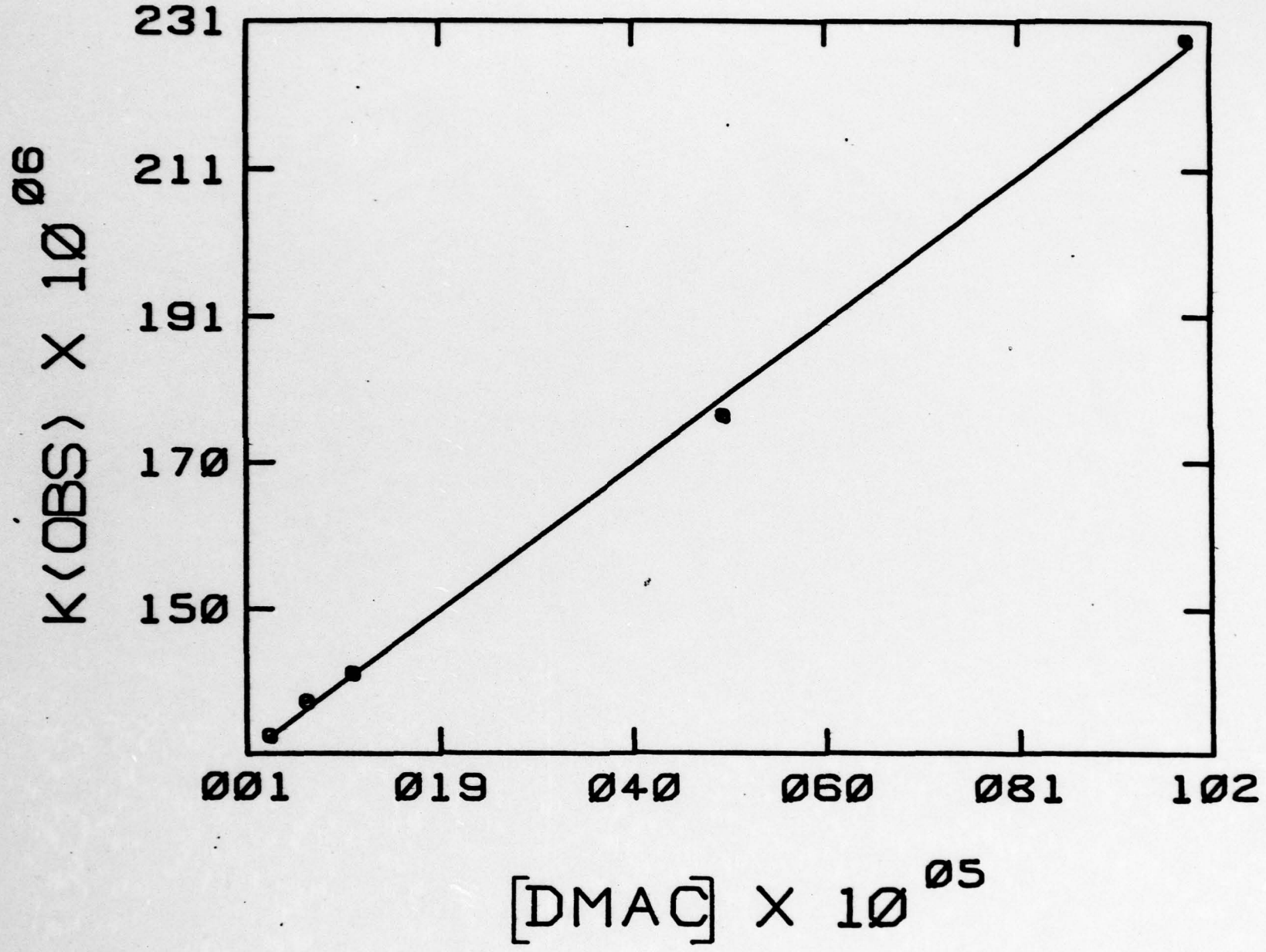
257
260
264
268
272
1/(TEMP.) °K X 10^05

Figure 2.


231
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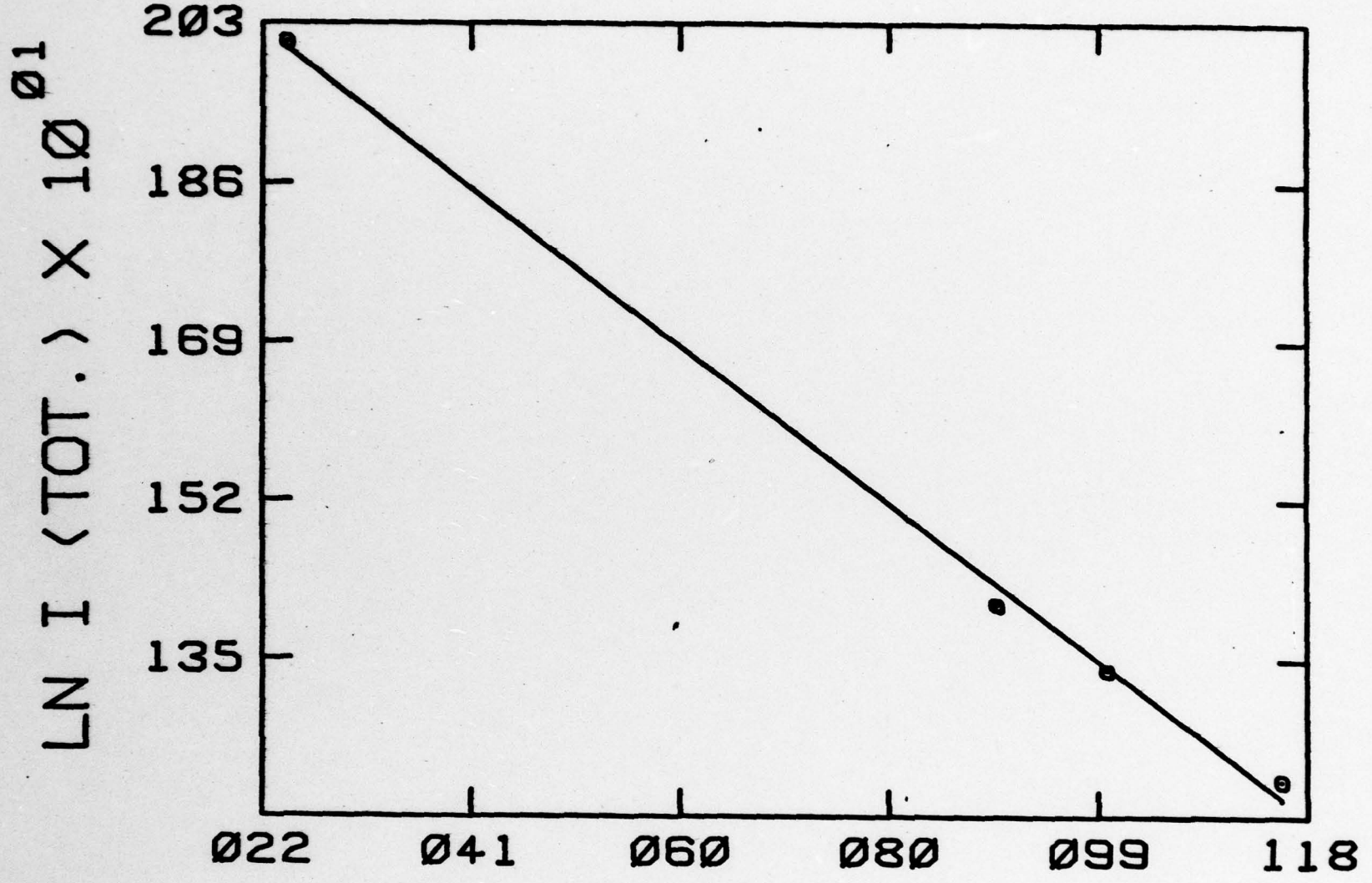
[DMAC] X 10^05

Figure 3.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