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# MECHANISM AND RATE CONSTANTS FOR 1,3-BUTADIENE DECOMPOSITION

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Data on the decomposition of 1,3-butadiene have been analyzed. The numerous isomerization processes that have recently been proposed as additional channels for decomposition have been considered. Energy transfer effects have been taken into account through the solution of the time-dependent master equation. We confirm recent supposition that direct formation of ethylene and acetylene is a major reaction channel during the thermal decomposition of 1,3-butadiene. The isomerization to 1,2-butadiene and its subsequent decomposition to form propargyl and methyl is the next most important process. Almost no vinyl radicals are produced. The formation of the isomerization products, in contrast to those from the initial reactant, is generally characterized by long transients before the attainment of a steady state. Standard methods of treating processes where such reactions are important must be carefully analyzed. The calculations are calibrated with experimental results. It proved not to be possible to fit simultaneously all the experimental observations with the model. Rate expressions for the major decomposition and isomerization channels are presented.

## Introduction

This paper is concerned with the decomposition of 1,3-butadiene at combustion temperatures. This compound is an important component in high-temperature organic systems. It is prototypical of the polyunsaturated compounds that are the intermediates in the formation of aromatics and ultimately soot. There has been considerable confusion regarding its mechanism and rates of decomposition. It appears that this is a very complex process involving simultaneously a variety of isomerization and bond-breaking processes. The general situation is compounded by the reactions occurring in temperature regions where energy transfer is of importance. Hence, it is difficult to use the experimental results to project data to conditions different from those used in the measurements. In this paper, we summarize the present experimental situation on the initial processes in 1,3-butadiene decomposition and then take into account intermolecular energy transfer effects (which are always present in high-temperature systems) on the basis of a solution of the master equation to determine mechanisms and rate constants over extended temperature and pressure ranges. All the decomposition and isomerization channels are considered and specific rates determined via Rice–Ramsperger–Kassel–Marcus calculations [1,2]. Particular interest is focused on deriving a set of high-pressure rate expressions. It is well known that such data represent the key inputs for the analysis of chemical activation processes. This is another important aspect of the decomposition of compounds such as 1,3-butadiene. In addition to thermal decomposition, it is also necessary to consider the decomposition of the hot radicals formed as a result of their combination. Finally, in soot formation mechanisms, models have been built using $C_2$ and $C_3$ unsaturates [3,4]. The reactions of interest in this work provide a means of conversion between the two types of compounds.

Although the general principles for treating multichannel decompositions are well understood, there has been very little work on the solution of real problems. Thus, aside from the direct interest, another aim of this study is to gain some experience on treating such systems and the methodology for presenting results. It will become clear that the conversion of such data into the format for standard simulation programs remains a serious problem.

In the high-temperature decomposition of highly unsaturated organic compounds, the general situation as epitomized by butadiene decomposition is probably the rule rather than the exception. Most standard treatments of decompositions deal with a single-channel process and use a modified strong collision approach [1]. This is not extensible to multichannel decompositions. The master equation approach is the only valid procedure. The modified strong collision approach is in fact a simplification derived from the solution of the master equation [2]. A very important consideration is how energy transfer effects will be manifested in such multichannel decomposition processes. It is obvious that in the case of multichannel decomposition reactions, the

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upper channels will be severely affected by the presence of lower-energy reaction channels. This will lead to a stronger pressure-dependent rate constant, since the lower channel will lead to a drastic reduction of the population at higher energies. Thus, the limiting rate constant at low pressures, $k(0)$, is no longer solely dependent on the molecular properties and the amount of energy transferred per collision. It does not even have to be second order. At least formally, it is no longer possible to present results on the basis of the Troe formalism [5]. The situation is made even more complex by the presence of reversible isomerization processes. Activated molecules are not removed from the system. Instead, they can return to the reactant pool. This paper thus treats the most general case and seeks to extract from the methodology information on the nature of the initial steps in 1,3-butadiene decomposition.

The paper will begin with a brief description of our master equation treatment of such systems. We will then summarize the available experimental data and use them to provide the input parameters for the present analysis. An attempt will be made to make a best possible fit to the experimental results. This will then lead to recommendations for rate constants for the unimolecular decomposition of 1,3-butadiene and the branching ratios over extended temperature and pressure ranges.

## Master Equation Treatment

The present treatment is derived from the formulation of Gilbert and Smith [2]. Our implementation is, however, based on the solution of the time-dependent master equation [6] using the Householder and QR algorithms for tridiagonalization and the determination of eigenvalues and functions. This leads to the determination of the complete time evolution, beginning with the initial transient and ending with the steady-state distribution, of the system. Rate constants have meaning only under the latter conditions. The details of our approach have been summarized in a series of recent papers [6–8]. A Windows-based program has been prepared. It can be considered a bridge between experimental data covering limited ranges of conditions and the extensions necessary for correct application in simulations. Earlier studies were concerned with reactions with low barriers and where isomerization processes are also contributing. The main focus was the applicability of the steady-state approximation. This study is focused on a very stable molecule. Reaction barriers are high, and there should certainly be large ranges where "normal" behavior occurs. Our interest is mainly on the "normal" chemistry process and its range of applicability.

## Past Work

Table 1 contains a summary of applicable experimental results on the initial steps in 1,3-butadiene decomposition. The situation is not completely satisfactory. There are problems that no amount of analysis can resolve. The chief issue is the question of reaction mechanism. Kiefer and coworkers [9,10] measured rates of decomposition using the laser schlieren and laser flash-absorption method. Due to the short time available for reaction, these are the most unambiguous experimental observations in terms of accessing initial processes. There are no complications from the subsequent chemistry. The uncertainty is on the nature of this process. Kiefer and coworkers [9] assumed that the decomposition to two vinyl radicals is the primary reaction step. They obtained a value for the heat of formation of vinyl radicals that is now known to be much too low [11]. Their rate constants are at least two orders of magnitude larger than needed to accommodate the thermochemistry that is consistent with the creation of vinyl radicals. The original laser schlieren measurements are related to the rate of heat release. Thus, built into the results are the assumed chemistry and the corresponding thermochemistry. If the main reaction involves the formation of ethylene and acetylene, then their laser schlieren–derived rate constants should be raised by a factor of 2.5. An examination of their subsequent results using laser flash absorption suggests that they are compatible with this change.

Skinner and Sokolski [12] studied 1,3-butadiene decomposition in single-pulse shock tube experiments. At the lower temperatures, they obtained equal yields of ethylene and acetylene. This rough equality of the two major products also appears to have been observed by Hidaka et al. [13] and Colket [14]. Benson and Haugen [15] analyzed butadiene decomposition using the data of Skinner and Sokolski [12]. They postulated a chain mechanism, with the initial step involving the formation of two vinyl radicals. With the newer high heats of formation of the vinyl radical, this is no longer tenable. The relative unimportance of a vinyl formation mechanism is experimentally confirmed by the results of Rao et al. [16]. They carried out shock tube experiments at high dilutions under pressure and temperature conditions similar to those used by Kiefer et al. [9] in their laser schlieren studies. The rates of hydrogen-atom production were at least two orders of magnitude lower than the rate constant for butadiene decomposition determined by Kiefer et al. [9].

Recently, Hidaka et al. [13] carried out 1,3-butadiene decomposition studies in a series of shock tube experiments. Various diagnostics were employed, and a detailed mechanism was developed. To accommodate their observations, direct formation of ethylene and acetylene was proposed. Their mechanism

TABLE 1
Rate expression used in carrying out calculations and comments justifying their selection

| Reaction | Rate Expression $(\mathrm{s}^{-})$ | Comments |
|---|---|---|
| $1,3\text{-}C_4H_6 = C_2H_4 + C_2H_2$ | $2.8 \times 10^{17}\exp(-46700/T)$ | Best fit of experimental data; present results |
| $1,2\text{-}C_4H_6 = C_3H_3 + CH_3$ | $5 \times 10^{15}\exp(-37{,}700/T)$ | From estimated rate constants for reverse and thermodynamics [20,22] |
| $2\text{-}C_4H_6 = 2\text{-}C_4H_5\text{-}1 + H$ | $1.5 \times 10^{16}\exp(-47{,}000/T)$ | Based on measured rate constant for combination of allyl + H from Hanning-Lee and Pilling [25] |
| $c\text{-}C_4H_6 = C_2H_4 + C_2H_2$ | $1.4 \times 10^{15}\exp(-36{,}300/T)$ | Estimate (see text) |
| $1,3\text{-}C_4H_6 = 1,2\text{-}C_4H_6$ | $8 \times 10^{13}\exp(-37{,}700/T)$ | Derived from the reverse reaction; see below and the thermodynamics |
| $1,2\text{-}C_4H_6 = 1,3\text{-}C_4H_6$ | $2.5 \times 10^{13}\exp(-36{,}600/T)$ | Estimate of Hidaka et al. [26] (confirmed by Tsang et al. [28] and Wang et al. [23]) |
| $1,3\text{-}C_4H_6 = 2\text{-}C_4H_6$ | $2.1 \times 10^{13}\exp(-36{,}600/T)$ | Derived from the reverse reaction; see below and the thermodynamics |
| $2\text{-}C_4H_6 = 1,3\text{-}C_4H_6$ | $3 \times 10^{13}\exp(-32{,}700/T)$ | From Hidaka et al. [27] |
| $1,3\text{-}C_4H_6 = c\text{-}C_4H_6$ | $4.2 \times 10^{11}\exp(-21{,}500/T)$ | Derived from the reverse reaction and the thermodynamics [19] |
| $c\text{-}C_4H_6 = 1,3\text{-}C_4H_6$ | $1.2 \times 10^{13}\exp(-16{,}200/T)$ | From review of Benson and O'Neal [22] |
| $1,2\text{-}C_4H_6 = 2\text{-}C_4H_6$ | $7 \times 10^{12}\exp(-31{,}720/T)$ | Derived from the reverse reaction; see below and the thermodynamics |
| $2\text{-}C_4H_6 = 1,2\text{-}C_4H_6$ | $3 \times 10^{13}\exp(-33{,}700/T)$ | From Hidaka et al. [26] |
| $1,3\text{-}C_4H_6 = 2\text{-}C_2H_3$ | $2.8 \times 10^{17}\exp(-56{,}300/T)$ | Based on measured rate constant for reverse process from Fahr et al. [24] and the thermodynamics |
| $1,3\text{-}C_4H_6 = 1,3\text{-}C_4H_5\text{-}2 + H$ | $4.4 \times 10^{15}\exp(-95{,}100/RT)$ | Same as for $2\text{-}C_4H_6 = C_4H_5\text{-}2 + H$ |

*Note:* Thermodynamic properties were derived on the following basis: (a) stable compounds from Stull et al. [18] except for cyclobutene, which are from Wiberg and Fenoglio [19]; (b) vinyl are from Tsang and Hampson [21], with heat of formation from Kaiser and Wallington [11]; (c) propargyl are from Tsang [20]; (d) $1,3\text{-}C_4H_5\text{-}2$ and $2\text{-}C_4H_5\text{-}1$ estimated from prescription given by Benson and O'Neal [22].

contains the first inclusion of isomerization processes. No account was taken of pressure dependencies. The rate constants for the direct ethylene and acetylene formation route are considerably smaller than the results of Skinner and Sokolski [12] and to a lesser degree the adjusted laser schlieren results of Kiefer et al. [9,10]. Finally, Thorn et al. [17] carried out vinyl radical combination studies and postulated cyclobutene as a product. Since the rate constant for cyclobutene to 1,3-butadiene is well established [18], the remaining issue is the decomposition of cyclobutene to ethylene and acetylene.

## Analysis

The data in Table 1, a listing of high-pressure rate expressions, form the basis for the present treatment of 1,3-butadiene decomposition. Also included are some ancillary notes that provide the justification for their selection. We follow Hidaka et al. [26,27] in including the isomerization processes. We have confirmed their results for 1,2-butadiene conversion to 1,3-butadiene from our own experiments [28]. They have also been confirmed by the theoretical work of Wang et al. [23]. The rate expressions for bond cleavages were determined from the equilibrium constant and the reverse combination process. It follows the general pattern of A factors that have been determined from single-pulse shock tube studies on thermal decompositions [29]. Thorn et al. [17] assigned an activation energy for cyclobutene decomposition equal to that for cyclobutane decomposition (262 kJ/mol). A more likely value will be 45 kJ/mol higher and is based on the increase in bond energies in hydrocarbons as a result of vinyl substitution. The selected A factor is a factor of 2 smaller than that for cyclobutane. Hidaka et al. [13] were not able to account for their results without a direct channel for the creation of ethylene and acetylene. They did not include in their mechanism the channel involving cyclobutene formation. With the value postulated by Thorn et al. [17] for the activation energy, it is almost possible to fit the experiments.

The direct formation of ethylene and acetylene from 1,3-butadiene is a controversial question. Theoretical calculations by Wang [30] provide evidence for this reaction to proceed through a vinylidine-type intermediate. Vinylidine will convert rapidly to form acetylene. The number given here is the

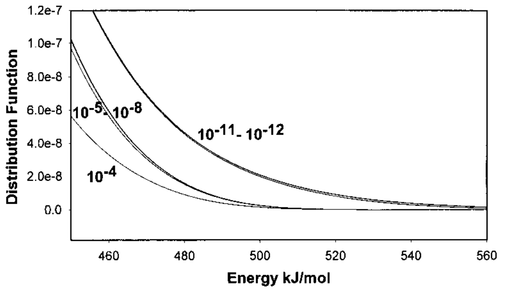

FIG. 1. 1,3-butadiene distribution function at various times at 1600 K and 1 bar. The numbers represent times (in seconds) after initiation of experiments.

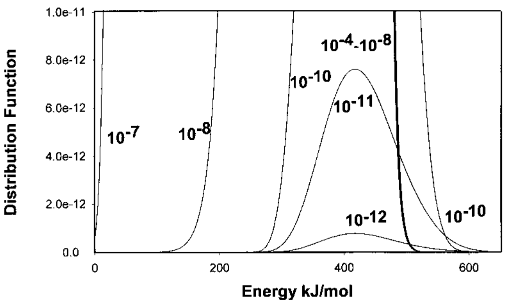

FIG. 2. 1,2-butadiene distribution function at various times at 1600 K and 1 bar. The numbers represent times (in seconds) after initiation of experiments.

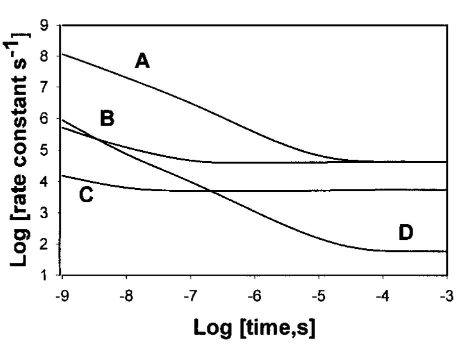

FIG. 3. Rate constants as a function of time for decomposition processes involved in 1,3-butadiene decomposition at 1600 K and 1 bar. (A) 1,2-butadiene = propargyl + methyl; (B) 1,3-butadiene = ethylene + acetylene; (C) cyclobutene = acetylene + ethylene; (D) butyne-2 = butynel-2 + H.

value required to fit experimental data. An important uncertainty is whether there is a barrier for the reverse process. The theoretical calculations seem to indicate its existence. Nevertheless, the large A factor is characteristic of a reaction without barriers. It is known that as long as a correct rate expression is used at a particular temperature, the present type of calculation is insensitive to the details of the transition state. Problems may arise when one seeks to extrapolate the results to different temperatures. Reactions without barriers (such as for bond breaking) lead to A factors and activation energies that decrease with temperature [24]. The reverse is true for those with barriers. The present approach is therefore restricted to the higher temperature range.

The transition state structures and energetics are derived from the A factors and activation energies given in Table 1. For the bond-breaking reactions, we adopt the procedure given in the earlier work [31]. For the reactions with barriers, the transition state is based on the assumed reaction coordinate and increasing or decreasing the frequencies of modes applicable to either tightening or loosening the molecular structure. Earlier, we remarked on the insensitiveness of energy transfer effects to details of the transition state as long as the experimental A factor is reproduced. The analysis requires an assignment of the contributions of energy transfer to the decomposition process. For hydrocarbons, it appears that this can be summarized in terms of a step size down and the values are not particularly sensitive to structure. We have assumed a value of 400 $cm^{-1}$ at 1200 K and increasing linearly to 600 $cm^{-1}$ at 1800 K [15]. Variations of these values will require adjusting the transition state properties if the same data are to be fitted. The transport properties are those for 1,3-butadiene.

## Results and Discussion

Figure 1 contains calculated results on 1,3-butadiene distribution functions as a function of time. After an initial transient period, the distribution function assumes a steady-state value. The final curve is due to the disappearance of the reactant. Fig. 2 contains the distribution functions for 1,2-butadiene, which are considerably different from those for 1,3-butadiene. The time evolution of the distribution functions is characteristic of a chemical activation experiment. One begins with a small number of activated molecules from 1,3-butadiene. As more molecules cross the barrier, the lower-energy levels are populated. It is apparent that over a period of time, there is a steady state at the high-energy end of the distribution function. However, the population of the lower levels is still increasing. The consequences in terms of rate constants can be seen in Figs. 3 and 4. It can be seen that, except possibly for

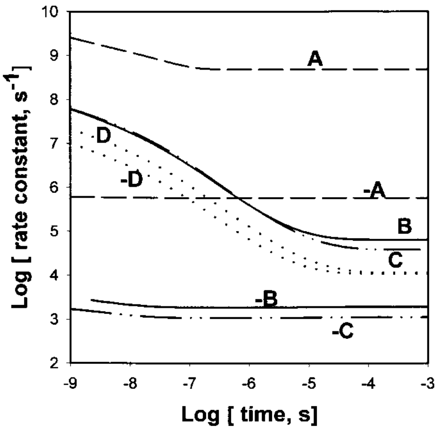

FIG. 4. Rate constants as a function of time for isomerization processes involved in 1,3-butadiene decomposition at 1600 K and 1 bar. (A, −A) cyclobutene = 1,3-butadiene; (B, −B) 1,2-butadiene = 1,3-butadiene; (C, −C) 2-butyne = 1,3-butadiene; (D, −D) 2-butyne = 1,2-butadiene.

cyclobutene, when one begins with the original molecule, steady state is achieved much faster than for the isomeric product. The extension of the transient region into increasingly longer times obviously has very serious consequences. It means that the number of regions where it is possible to describe the phenomenon in terms of rate constants in the traditional sense (constant with time) is decreased. However, the plot is logarithmic in nature. Unless the transient behavior extends to regions where significant conversion occurs, it is not of concern. Cyclobutene isomerization is characterized by much lower barriers for reaction. The much shorter transient behavior is consonant with the shorter time needed to fill the well with molecules. The difference between the transient behavior of rate constants for decomposition of the initial isomer and those that are formed in the course of the reaction is a reflection of the difference in the approach to the steady state.

Fits of our results to experimental observations can be found in Table 2. The laser schlieren results are fairly consistent with the findings of Skinner and Sokolski [12] at the lowest temperatures. Although calculated hydrogen yields are an order of magnitude lower than those of Rao et al. [16], this further indicates that hydrogen atoms cannot be the chain carrier. These results strongly support the non-chain nature of 1,3-butadiene decomposition. With the formation of propargyl, the system is probably self-inhibiting.

Figure 5 contains typical data on the distribution of products from 1,3-butadiene decomposition. Direct formation of ethylene and acetylene is the major channel. However, at low extents of reaction, the other channels make more contributions. At the highest temperatures, the second most important product is from 1,2-butadiene decomposition. Together, these two channels contribute about 90% of the product. Contributions from the cyclobutene decomposition channel are small. A comparison of the data in Figs. 4 and 5 shows that at the beginning of the decomposition process the rate constant for 1,2-butadiene decomposition is in fact significantly larger than the steady-state value. This is in contrast to the situation for 1,3-butadiene decomposition, where it is possible to characterize the reaction in the standard manner. From a combustion point of view, an important mechanistic result is that butadiene decomposition leads to the formation of propargyl and methyl instead of two vinyl radicals. This result is consistent with the observations of Kubitza

TABLE 2
Summary of experimental results and comparison with recommendations

| Reference | Conditions<br>Pressure (bar) | <br>Temp. (K) | Rate Constants ($s^{-1}$) | Present Recommendations ($s^{-1}$) |
|---|---|---|---|---|
| Skinner and Sokolski [12] | 5 | 1207 | 8 | 4 |
| Kiefer et al. [9,10] | 0.7 | 1600 | 5457 (total) | 6000<br>2000 (without main reaction involving ethylene and acetylene formation) |
| | | 1800 | 70,000 | 50,000<br>15,000 (without main reaction involving ethylene and acetylene formation) |
| Hidaka et al. [13] | 2 | 1200 | 0.57 | 3 |
| | | 1600 | 1855 | 6500 |
| Rao et al. [16] | 0.5 | 1600 | 40 (H-atom product) | 6 |

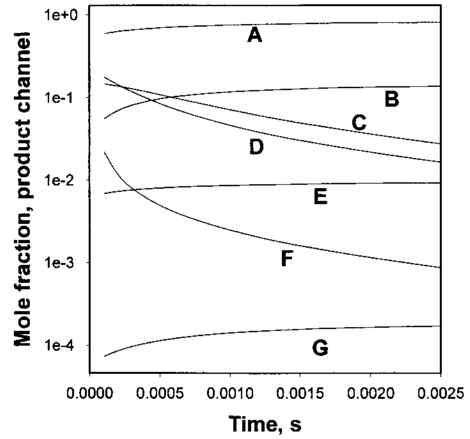

FIG. 5. Branching ratios at 1600 K and 1 bar as a function of time during 1,3-butadiene decomposition in terms of channels producing various products. (A) ethylene + acetylene (from 1,3-butadiene); (B) propargyl + methyl (from 1,2-butadiene); (C) 2-butyne; (D) 1,2-butadiene; (E) ethylene + acetylene (from cyclobutene); (F) cyclobutene; (G) butynel-2 and H (from 2-butyne).

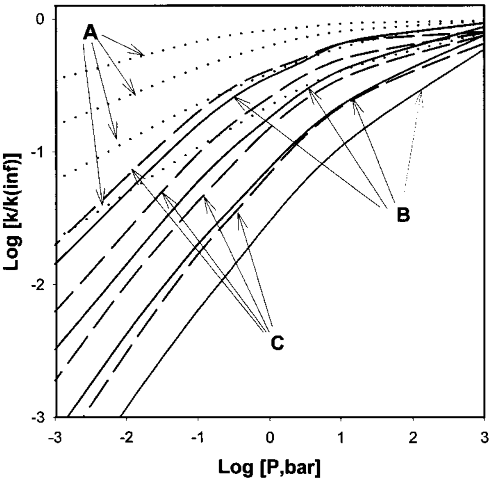

FIG. 6. Pressure dependence (with steady-state distributions) for the important reactions during 1,3-butadiene decomposition. (C) 1,3-butadiene = ethylene and acetylene (solid line); (B) 1,2-butadiene = propargyl + methyl (dashed line); (A) 1,3-butadiene ⇔ 1,2-butadiene (dotted line) at 1200, 1400, 1600, and 1800 K, beginning from the top.

[32] regarding the presence of propargyl during vinyl combination and has implications for soot formation mechanisms involving butadiene. The formation of ethylene and acetylene probably has much smaller consequences since they are undoubtedly already present in the system.

Figure 6 contains fall-off behavior ($k/k_\infty$, where $k$ is from the master equation solution and $k_\infty$ is from Table 1) over a number of temperatures. The recommended rate expressions for the four main reactions in 1,3-butadiene decomposition at 1 bar are

$$k(\text{1,3-C}_4\text{H}_6 = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2)$$
$$= 10^{88.62}T^{-20.85}\exp(-66{,}900/T)\text{s}^{-1}$$
$$k(\text{1,2-C}_4\text{H}_6 = \text{C}_3\text{H}_3 + \text{CH}_3)$$
$$= 10^{87.97}T^{-20.83}\exp(-61{,}400/T)\text{s}^{-1}$$
$$k(\text{1,3-C}_4\text{H}_6 = \text{1,2-C}_4\text{H}_6)$$
$$= 10^{75.34}T^{-17.56}\exp(-58{,}270/T)\text{s}^{-1}$$
$$k(\text{1,2-C}_4\text{H}_6 = \text{1,3-C}_4\text{H}_6)$$
$$= 10^{88.62}T^{-20.85}\exp(-66{,}860/T)\text{s}^{-1}$$

The peculiar form of the rate expressions is due to the reaction being in the pressure-dependent region. Results have been presented in this form since, as noted earlier, the standard formulation [5] developed for single-channel processes is no longer valid. Over narrow ranges, one could presumably still force a fit. The isomerization reactions are closer to the high-pressure limit. Of course, the departures from the high-pressure limit, at least initially, are due to completely different phenomena. There are other interesting questions regarding the nature of the steady state. They impinge on possibilities of simplifying the treatment and presentation of the results and are beyond the scope of the present work. For the present, it is necessary to depend on the expressions at 1 bar and for different pressures, interpolating the data in Fig. 6.

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