AIP | The Journal of Chemical Physics

# Kinetics of the Thermal and Nitric OxideCatalyzed Geometrical Isomerization of cis and transPropylene1d 1

M. C. Flowers and Neville Jonathan

Citation: The Journal of Chemical Physics **50**, 2805 (1969); doi: 10.1063/1.1671467
View online: http://dx.doi.org/10.1063/1.1671467
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/50/7?ver=pdfcov
Published by the AIP Publishing

---

---

$A+B\sin 2\lambda+C\cos 2\lambda$, where $A$, $B$, and $C$ are constants only depending on $\alpha$, $\beta$, and $\gamma$ and a phase angle. More generally, for a rotation around any crystal axis the following relation is found:

$$\Delta H_j(\lambda)=\tfrac{1}{2}(\Lambda_{ii}'+\Lambda_{kk}')\pm\Lambda_{ik}'\sin 2\lambda+\tfrac{1}{2}(\Lambda_{ii}'-\Lambda_{kk}')\cos 2\lambda. \quad (1)$$

There are thus two solutions possible if $\Lambda_{ik}'\neq 0$. The above derived relation is valid for one tensor $\Lambda'$ in the crystal axes system. When there are four $\Lambda'$ tensors in the crystal axes system related by three $C_2$ axes, it is easy to show that two of them will give the plus sign and the other two the minus sign. However, it is not known which tensors give plus and which give minus signs. In the case under investigation two ESR splittings will be observed which are connected through Relation (1). As is evident from this relation, since $\Delta H_j(90°+\lambda)=\Delta H_j(90°-\lambda)$, there will be a mirror relationship of the ESR splittings observed around any crystal axis. This was shown in Figs. 7 and 8.

---

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 50, NUMBER 7 1 APRIL 1969

# Kinetics of the Thermal and Nitric Oxide-Catalyzed Geometrical Isomerization of *cis*- and *trans*-Propylene-1-$d_1$

M. C. FLOWERS AND NEVILLE JONATHAN
*Department of Chemistry, The University, Southampton, England*

(Received 16 October 1968)

The thermal *cis–trans* isomerization of propylene-1-$d_1$ has been studied from 460°–541°C over a pressure range of 3–250 mm Hg in a Pyrex reaction vessel. The reaction below 20 mm Hg is homogeneous and unimolecular but just in the pressure-dependent region, $k_{\infty,cis-trans}(\text{sec}^{-1})=10^{13.16}\exp(-61\,300/RT)$. Above 20 mm a second-order reaction begins to contribute to the isomerization rate. The nitric oxide-catalyzed isomerization of *cis*-propylene-1-$d_1$ was studied between 398° and 452°C at propylene pressures of between 8 and 22 mm. Hg and NO pressures of 5–35 mm Hg. The reaction is first order in propylene and nitric oxide. The second-order rate constant is given by $k(\text{liters mole}^{-1}\cdot\text{second}^{-1})=10^{8.27}\exp(-27\,900/RT)$.

## INTRODUCTION

It has become apparent that many of the *cis–trans* isomerizations of substituted ethylenes studied and originally thought to be homogeneous unimolecular reactions were proceeding via a radical mechanism.[1] The number of genuine examples of the geometrical isomerization of substituted ethylenes occurring via a homogeneous unimolecular path is small (see Refs. 1 and 2 for examples). In all of these cases it appears that the measured frequency factor is in agreement with a mechanism in which isomerization occurs via a twisting of the double bond with the molecule remaining in a singlet electronic state, rather than via excitation to a triplet state which, on reverting to the ground state, results in isomerization. The present study provides a further example of an authentic homogeneous unimolecular *cis–trans* isomerization with the frequency factor in agreement with the singlet mechanism.

## EXPERIMENTAL

### Materials

### *Preparation of cis- and trans-Propylene-1-$d_1$*

The method used was the one described by Farina and Peraldo.[3] Pure (>98%) *cis*-(bp$_{25}-18$°C) and *trans*-(bp$_{25}-13$°C) bromopropene were obtained by fractional distillation of the mixed isomers using a 22-in. Podbielniak-type column operated with a head temperature of about −20°C. A catalyzed geometrical isomerization on the column was suppressed by addition of small amounts of ethanol to the mixture. Replacement of bromine by deuterium was effected by reaction with lithium at −12°C in ether solution under an atmosphere of nitrogen and reaction of the compound formed with $D_2O$. Ether was removed by trap-to-trap distillation. Mass-spectrometric, infrared, and vapor phase chromatographic analysis gave the following results:

*cis*-propylene-1-$d_1$ 5.4% *trans*-$d_1$; 2.6% $d_0$; 0.1% other products,
*trans*-propylene-1-$d_1$ 2.8% *cis*-$d_1$; 3.2% $d_0$; 0.3% other products.

The NMR spectra run on 10% solutions in carbon tetrachloride confirmed the assignment of the *cis* and *trans* configurations.

### *Preparation of Methane*

Methane (Matheson C.P. grade) was degassed by pumping the liquid for several seconds followed by vaporization. This cycle was repeated at least 10 times.

---

[1] R. B. Cundall, Progr. Reaction Kinetics **2**, 165 (1964).
[2] M. C. Lin and K. J. Laidler, Can. J. Chem. **46**, 973 (1968).
[3] M. Farina and M. Peraldo, Gazz. Chim. Ital. **90**, 973 (1960).

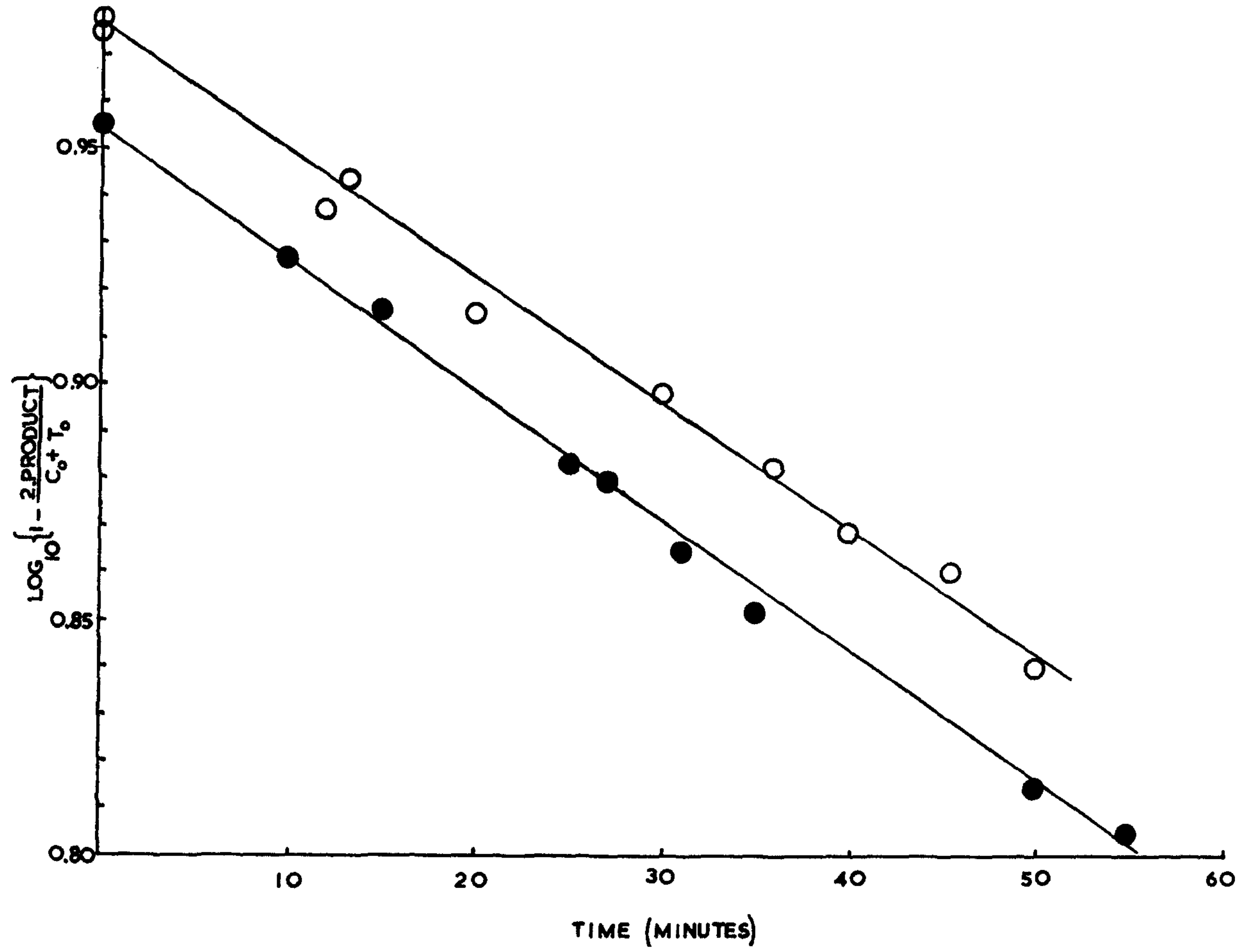


FIG. 1. First-order plot for the thermal isomerization of *cis*-propylene-1-$d_1$ at 496.8°C and *trans*-propylene-1-$d_1$ at 496.7°C. Abscissa, time (minutes); ordinate, $\log_{10}\{1-[2\text{ Product}/(C_0+T)]\}$. Initial reactant: ●, *cis*-propylene-1-$d_1$; ○, *trans*-propylene-1-$d_1$.

### *Preparation of Nitric Oxide*

Nitric oxide (Air Products) was thoroughly degassed and purified by repeated trap-to-trap distillation (−160° to −196°C).

### Apparatus

Pyrolyses were carried out in a spherical, "aged," Pyrex reaction vessel (173 ml) immersed in a fused-salt (ternary eutectic of $NaNO_3/KNO_3/NaNO_2$) thermostat the temperature of which was maintained constant to ±0.1°C by a Sunvic RT 3R temperature controller. The "dead space" was 0.5% and corrections were applied to the measured rate constants for this. Temperatures were measured with a calibrated Pt/Pt–13% Rh thermocouple. For some runs an aged reaction vessel packed with short lengths (about $\frac{1}{4}$ in.) of glass tubing with fire-polished ends was used. The surface area–volume ratio of this vessel was 11.6 $cm^{-1}$ (i.e., 12.5 times that of the unpacked vessel).

Analyses were performed using a specially constructed 5-cm path-length minimum volume gas cell on a Grubb–Parsons GS2A infrared grating spectrometer. Empirical calibration curves were obtained for both *cis* and *trans* isomers at a number of wavelengths in the regions 10–10.5 $\mu$ and 12.5–13 $\mu$. Although the *trans* isomer absorbed strongly in the former region whereas the *cis* did so in the latter, there was in each case, a small contribution from the other isomer. The analyses were therefore made by the standard spectroscopic method for the case of a mixture of two compounds showing complete overlap of absorption spectra. The absorptivity was measured at three pairs of wavelengths from within the above two spectral regions and two simultaneous equations were solved to determine the percentage of each isomer present in the mixtures. The average of the three determinations was taken as the correct value.

### Procedure

The initial reactant was admitted to the reaction vessel from a gas pipette. After each run at 10 mm pressure or below, the entire sample was frozen into the infrared cell and the percentage composition determined. In cases where samples were at pressures in excess of 10 mm, only a sufficient sample to be equiva-

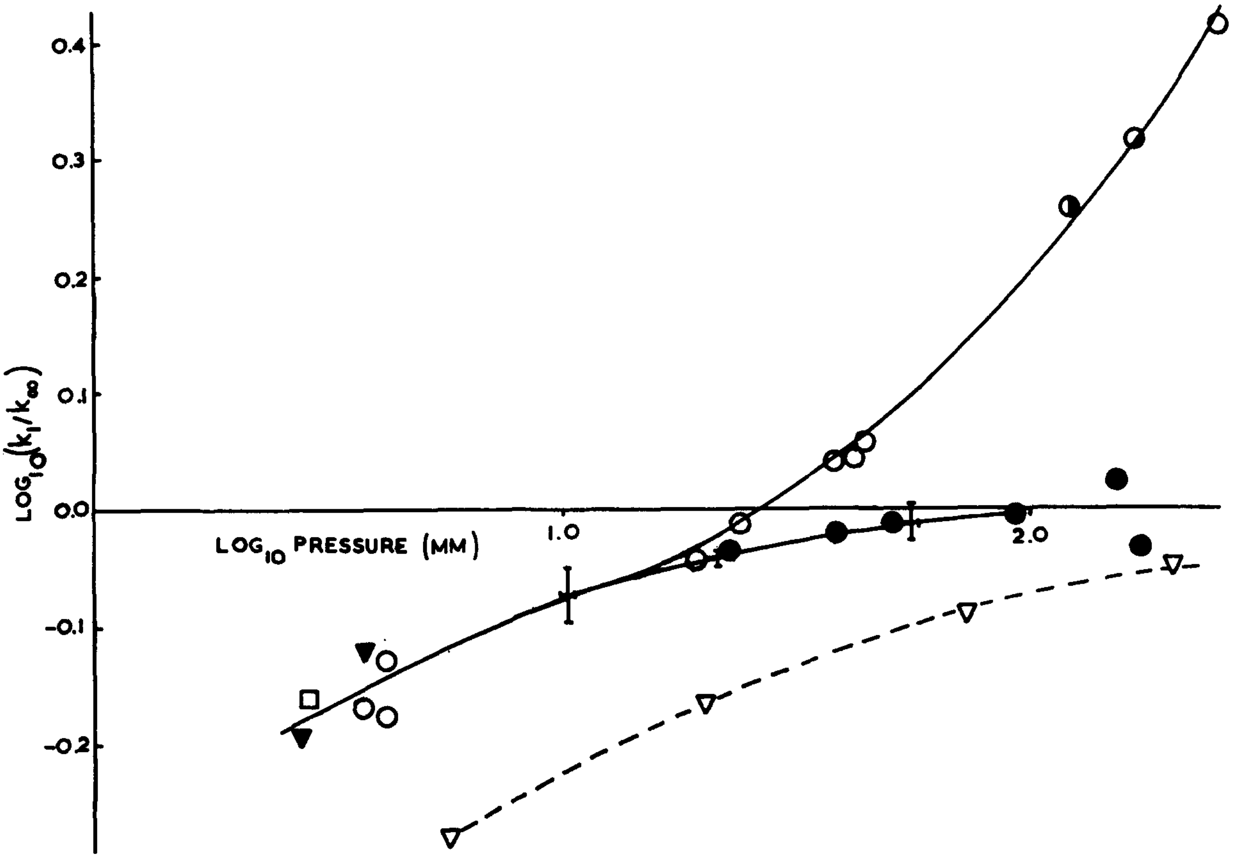


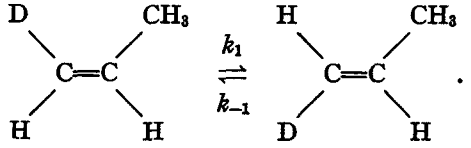
FIG. 2. Pressure dependence of rate of thermal isomerization of *cis*-propylene-1-$d_1$. Abscissa, $\log_{10}$ pressure (millimeters); ordinate, $\log_{10} k_1/k_\infty$. ○, Propylene alone at 482.4°C; ◑, propylene alone (prepyrolyzed starting material); ●, propylene+0.22×methane at 482.4°C; □, propylene alone at 496.7°C; ▼, propylene alone at 541.0°C; ✛, runs of 10 mm propylene+ .22× methane at 469.3°, 496.7°, 513.0°, 527.5°, and 541.0°C all fell within these limits; ▽, data for cyclopropane (Ref. 7).

lent to that of the 10-mm runs, was frozen into the infrared cell. Runs in which either methane or nitric oxide was added were made by addition of the second gas from a gas pipette at a measured short interval after the admission of propylene to the reaction vessel. This time delay was taken into account in the calculation of rate constants from the methane addition data but corrections in the case of nitric oxide were negligible. Methane was removed from the samples prior to infrared analysis by pumping on the sample at −196°C. Removal of nitric oxide from the samples did not alter the analysis data and so normally this was not done.

## RESULTS

### Uncatalyzed Reaction

The *cis–trans* isomerization of propylene-1-$d_1$ would be expected to obey reversible first-order kinetics,



The majority of runs were carried out using *cis*-propylene-1-$d_1$ as the initial reactant. The equilibrium constant for reaction would be expected to be close to unity. With this assumption, $k_1=k_{-1}$ and the integrated first-order rate equation becomes

$$\log_{10}[1-2T/(C_0+T_0)]=-2k_1t/2.303, \qquad (1)$$

where $C$ and $T$ are the concentrations of *cis*- and *trans*-propylene-1-$d_1$, respectively, at time $t$ and $C_0$ and $T_0$ are initial concentrations. Such a first-order plot was observed experimentally to be linear up to the highest conversions studied (40%) (see Fig. 1). Rate constants at 10 mm pressure from plots of this nature were determined at seven temperatures between 460° and 541°C. Rate constants were measured using *trans*-propylene-1-$d_1$ as initial reactant at 482.4° and 496.7°C and, after corrections for small pressure differences were, respectively, 1.02 and 1.03 times that of the corresponding value measured for the *cis* compound (i.e., identical within experimental error). First-order rate constants decreased with decreasing pressure of propylene down to the lowest accessible pressure (3 mm). Between 10 and 40 mm the first-order rate constant increased slowly with pressure. A much larger

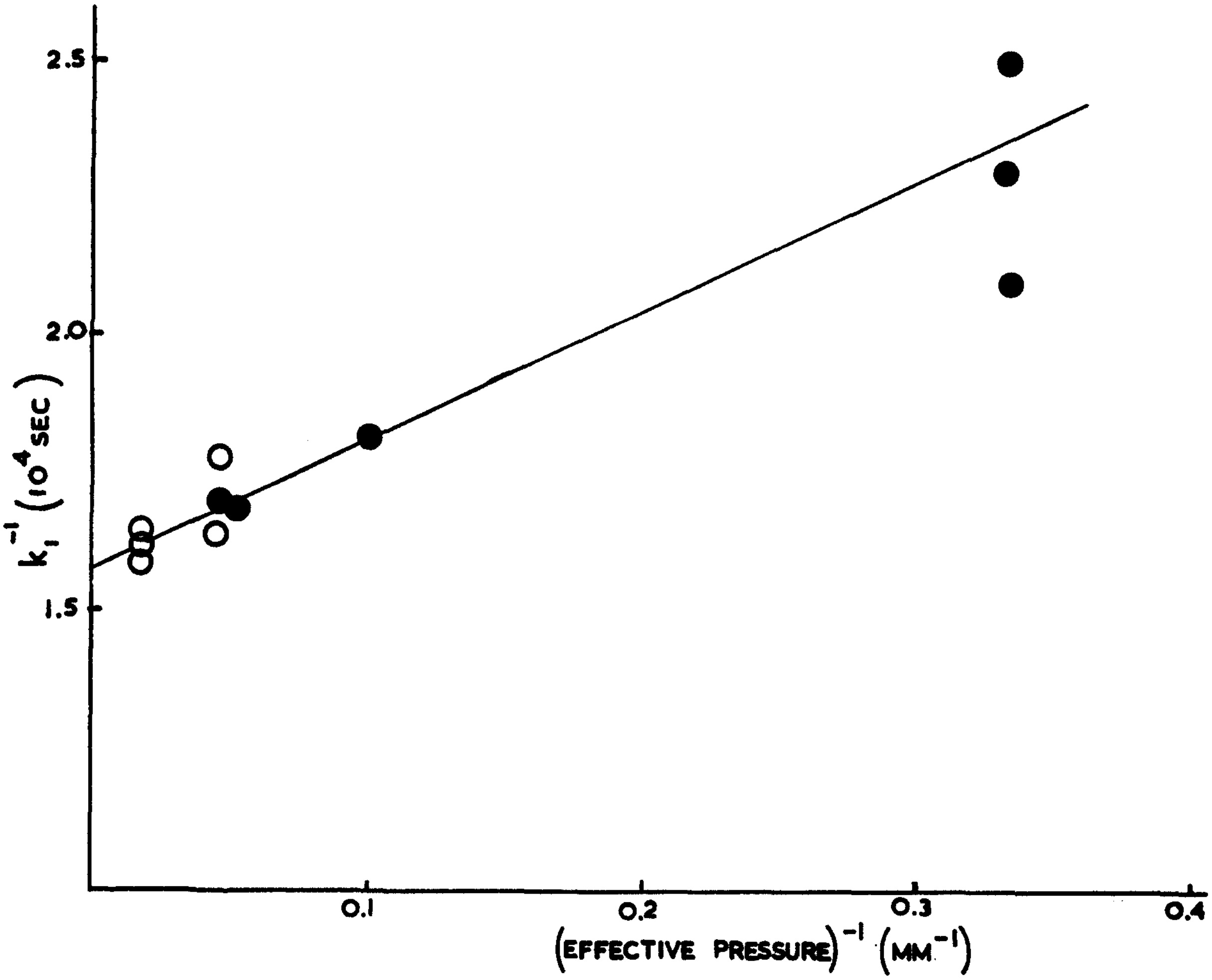


FIG. 3. Plot of (effective pressure)$^{-1}$ against $k_1^{-1}$ at 496.7°C. Abscissa, 1/effective pressure (millimeters$^{-1}$); ordinate, $1/k_1$($10^4$ sec). ●, propylene alone; ○, propylene+methane×0.22.

increase with pressure occurred above 40 mm (Fig. 2). No autocatalysis was observed even at the highest pressures studied as evidenced by virtually identical rate constants for reactions proceeding for different times and for an initial reactant that had been previously pyrolyzed. This is in contrast to the case of isomerization of 2-butene.[4]

By analogy with the isomerizations of 1,2-dideuterioethylene[5] and 2-butene this isomerization would be expected to be a first-order reaction in a pressure-dependent region. Runs were therefore performed with 10-mm *cis*-propylene-1-$d_1$ plus added methane as inert gas. First-order rate constants increased with increasing pressure but tended towards a limiting value at high methane pressures. Using the value of 0.22 obtained by Cundall and Palmer[4] for the collision efficiency of methane, an effective total pressure may be obtained (see Fig. 2). A plot of 1/(effective pressure) against $1/k_1$ is linear (Fig. 3) for propylene alone up to about 20 mm and with 10 mm propylene+methane up to the highest pressures studied (600 mm methane). Runs were performed at six different temperatures between 469° and 541°C for 10 mm propylene with 50 and 210 mm added methane. Plots of 1/(effective pressure) against $1/k_1$ were used to obtain values of $k_\infty$.[6]

Runs in the aged packed reaction vessel at 15 mm gave rate constants at 469.4° and 513.2°C which were 47% and 19%, respectively, faster than in the packed reaction vessel. This indicates some 3.8% and 1.6% heterogeneous reaction occurring in the unpacked reaction vessel at these temperatures. Rate constants measured are summarized in Table I and Arrhenius parameters are listed in Table II. Error limits are 95% certainty values. The Arrhenius plots were good straight lines with no indication of curvature.

---

[4] R. B. Cundall and T. F. Palmer, Trans. Faraday Soc. **57**, 1936, 2226 (1961).

[5] J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, J. Chem. Phys. **23**, 315 (1955).

[6] Theory predicts that this plot should be curved. The range of "fall off" covered is, however, small, and noticeable curvature is not to be expected. Comparison with the cyclopropane isomerization suggests that errors in the extrapolation procedure are not greater than the probable errors in the measurement of rate constants, i.e., ±4%.

TABLE I. Rate constants for the uncatalyzed geometrical isomerization of propylene-1-$d_1$.

| Temperature (°C) | $k_1$(10 mm)[a] ($10^{-5}$ sec$^{-1}$) | $k_1$(10+50 mm $CH_4$)[a] ($10^{-5}$ sec$^{-1}$) | $k_1$(10+210 mm $CH_4$)[a] ($10^{-5}$ sec$^{-1}$) | $k_\infty$ ($10^{-5}$ sec$^{-1}$) | $k_1$ (other pressures)[a] ($10^{-5}$ sec$^{-1}$) (pressure in second parentheses) |
|---|---|---|---|---|---|
| *cis*-propylene-1-$d_1$ | | | | | |
| 460.3 | 0.783(5) | | | | |
| 469.3 | 1.38(7) | 1.35(3) | 1.55(3) | 1.54 | |
| 469.4 | | | | 2.25[b](4) | |
| 482.4 | 2.54(7) | 2.75(3) | 2.87(3) | 2.97 | 3.29(4) (40 mm) |
| | | | | | 2.77(2) (20 mm) |
| | | | | | 2.07(2) (4.0 mm) |
| 496.7 | | 5.90(8) | 6.17(3) | 6.35 | |
| 496.8 | 5.38(8) | | | | 5.89(2) (20 mm) |
| | | | | | 4.40(3) (3.0 mm) |
| 513.0 | | 13.4(5) | 13.6(5) | 14.3 | |
| 513.1 | 11.5(6) | | | | |
| 513.2 | | | | 15.4[b](7) | |
| 527.5 | | 26.4(5) | 27.3(5) | 28.4 | |
| 527.6 | 24.1(6) | | | | |
| 541.0 | | 50.1(6) | 51.3(6) | 53.1 | 40.5(2) (3.7 mm) |
| | | | | | 34.1(2) (2.8 mm) |
| 541.3 | 42.5(8) | | | | |
| *trans*-propylene-1-$d_1$ | | | | | |
| 482.4 | 2.48(7) | | | | |
| 496.7 | 5.22(8) | | | | |

[a] Number of runs given in parentheses.

[b] Packed reaction vessel. Calculated values for $k_\infty$ from data at between 12 and 17 mm.

Using Fig. 2 it is possible to obtain the difference between the "true" first-order rate constant for the isomerization and the apparent first-order rate constant for runs at propylene pressures above 40 mm. This difference and its value when converted to a second-order rate constant, are shown in Table III. The second-order rate constant appears independent of pressure. Thus the increase in the reaction rate at high pressure appears to be due to a competing second-order reaction.

TABLE II. Arrhenius parameters for uncatalyzed *cis*–*trans* isomerization of *cis*-propylene-1-$d_1$.

| Pressure | $\log_{10}A$ (sec$^{-1}$) | $E_A$ (kcal mole$^{-1}$) |
|---|---|---|
| 10 mm | 12.25±0.41 | 58.2±1.4 |
| 10 mm+50 mm$CH_4$ | 12.92±0.18 | 60.4±0.6 |
| 10 mm+210 mm$CH_4$ | 12.58±0.46 | 59.2±1.6 |
| ∞ | 12.76±0.25 | 59.7±0.9 |
| ∞[a] | 12.85±0.21 | 60.1±0.8 |
| ∞[b] | 13.16±0.20 | 61.3±0.7 |

[a] Removing contribution from heterogeneous reaction.

[b] Removing contribution from heterogeneous reaction and from bimolecular reaction [assuming $k_{\text{bimol}}=10^{7.4}\exp(-30\,600/RT)$].

Chromatographic analysis at the end of some runs showed that side reactions were very small, much less than 0.2% for 40% conversion. Major byproducts identified were methane and ethylene in similar amounts. Products of higher molecular weight than propylene were detected but not identified. The percentage of byproducts increased as the total pressure increased. Thus a run at 482°C and 38 mm propylene at 38% conversion gave approximately 0.3% ethylene and 0.2% methane. The reaction mixtures resulting from runs above 40 mm propylene were collected and combined. Methane was pumped off and the ethylene separated by trap-to-trap distillation. Mass-spectrometric analysis at 12 eV showed the sample consisted of 29% $C_2H_2D_2$, 57% $C_2H_3D$, and 14% $C_2H_4$. Infrared analysis of this fraction indicated the presence of both *cis*- and *trans*-1,2-dideuterioethylene but 1,1-dideuterioethylene was not detected.

### Nitric Oxide-Catalyzed Isomerization

$$NO+\textit{cis}\text{-}C_3H_5D \overset{k_2}{\rightleftharpoons} NO+\textit{trans}\text{-}C_3H_5D. \qquad (2)$$

The NO-catalyzed isomerization was studied at four temperatures between 398° and 452°C using *cis*-

TABLE III. Second-order uncatalyzed rate of isomerization (482.4°C).

| $k_a$(apparent) ($10^{-5}$ sec$^{-1}$) | $k_t$(true) ($10^{-5}$ sec$^{-1}$) | $k_a-k_t$ ($10^{-5}$ sec$^{-1}$) | Propylene pressure (mm) | $k_{bimol}=$ $[(k_a-k_t)/\text{pressure}]$ (liters mole$^{-1}\cdot$second$^{-1}$) |
|---|---|---|---|---|
| 5.37 | 2.97 | 2.40 | 121.9 | $9.3\times10^{-3}$ |
| 6.11 | 2.97 | 3.14 | 167.6 | $8.8\times10^{-3}$ |
| 7.56 | 2.97 | 4.59 | 255.4 | $8.5\times10^{-3}$ |

propylene-1-$d_1$ pressures of between 8 and 22 mm and NO pressures of 5 to 35 mm. Plots of the first-order rate constant obtained using Eq. (1) against NO pressure were linear (Fig. 4). In each case a small positive intercept was found on the rate constant axis. The second-order rate constant $k_2$ for the isomerization (first order in propylene and first order in NO) was calculated from the slope of each of the above plots. These are listed in Table IV together with the intercept values. Error limits are 95% confidence values. Runs with propylene alone, interspersed between runs with NO, gave negligibly slow rates close to the values predicted from the Arrhenius parameters determined for the uncatalyzed reaction. Gas-chromatographic analysis did not detect any byproducts in these runs. Runs in the packed reaction vessel at 423.0°C gave a second-order rate constant 5.9% faster than in the unpacked vessel. Thus the heterogeneity in the unpacked vessel is approximately 0.5%. The intercept was unchanged. The rate of the nitric oxide-catalyzed isomerization can be expressed in Arrhenius form as

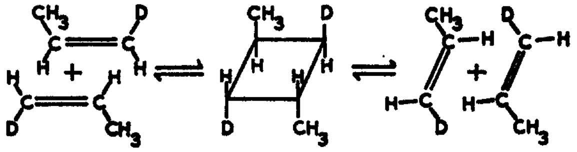
$$k_2(\text{liters mole}^{-1}\cdot\text{second}^{-1})=10^{(8.27\pm0.19)}\times\exp(-27\,900\pm600/RT).$$

## DISCUSSION

### Uncatalyzed Isomerization

Apart from a small amount of heterogeneous reaction, propylene-1-$d_1$ undergoes a unimolecular geometrical isomerization in the unpacked vessel at pressures below 20 mm. Support for this contention is given by the effect of inert gas, the dependence of the reaction rate on propylene pressure and by analogy with the *cis–trans* isomerizations of dideuterioethylene[5] and 2-butene.[4] The pressure dependence of the rate is seen to be similar to that found for the rate of isomerization of cyclopropane[7] (Fig. 2) but in the latter case falloff occurs at a pressure of approximately an order of magnitude higher. If $E_A/RT$ values for the two reactions were the same then the RRK theory would predict that the falloff would be shifted by a factor of $10^2$, i.e., the ratio of the frequency factors for the reactions. By using the data of Schlag, Rabinovitch, and Schneider[8] with a value of 11 for the number of effective degrees of freedom, the shift due to the difference in $E_A/RT$ was calculated to be about 0.25 log units. The residual 0.75 log units must presumably be explained in terms of a change in the number of effective degrees of freedom.

At pressures above 20 mm a second-order reaction begins to contribute to the rate of isomerization. A possible explanation of this is that propylene dimerizes to form various dimethylcyclobutanes. One of the dimethylcyclobutanes can decompose giving either two molecules of *trans*- or two molecules of *cis*-propylene-1-$d_1$,



If the possible differences in the rates of formation and

TABLE IV. Rate constants for NO-catalyzed isomerization of *cis*-propylene-1-$d_1$.

| Temperature (°C) | $k_2$ (liters mole$^{-1}\cdot$second$^{-1}$) | Intercept $k_1$ NO = zero ($10^{-5}$ sec$^{-1}$) |
|---|---|---|
| 362.5 | $0.0476\pm0.0035$ | $0.125\pm0.18$ |
| 398.3 | $0.153\pm0.007$ | $0.60\pm0.32$ |
| 423.0 | $0.321\pm0.018$ | $1.06\pm0.90$ |
| 423.0[a] | $0.340\pm0.010$ | $1.06\pm0.52$ |
| 452.1 | $0.732\pm0.036$ | $3.40\pm1.94$ |

[a] Packed reaction vessel.

TABLE V. Arrhenius parameters for thermal *cis–trans* isomerization of simple olefins.

|  | log$A$ (sec$^{-1}$) | $E_A$ (kcal mole$^{-1}$) | log$k_1$ (500°C) (sec$^{-1}$) | Reference |
|---|---|---|---|---|
| *trans*-$C_2H_2D_2$ | 13 | 65 | −5.4 | 5 |
| *cis*-$C_3H_5D$ | 13.2 | 61.3 | −4.1 | this work |
| *cis*-$C_4H_8$ | 14 | 62.4 | −3.6 | 4 |

---

[7] H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, Proc. Roy. Soc. (London) **A217**, 563 (1953); data from N. B. Slater, *ibid.* **A218**, 224 (1953).

[8] E. W. Schlag, B. S. Rabinovitch, and F. W. Schneider, J. Chem. Phys. **32**, 1599 (1960).

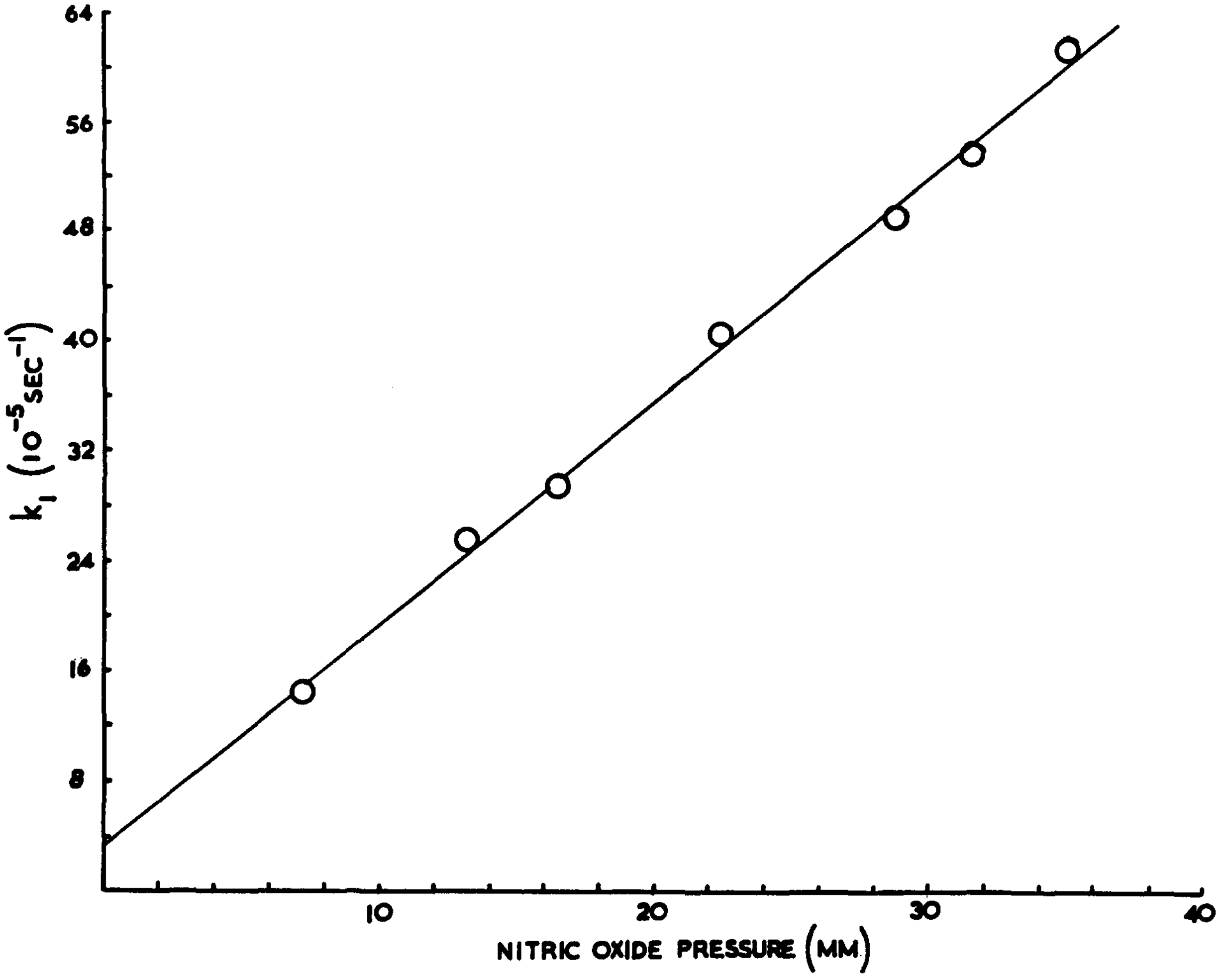


FIG. 4. Plot of first-order rate constant against nitric oxide partial pressure at 452.1°C. Abscissa: nitric oxide pressure (millimeters); ordinate: $k_1(10^{-5}\ \mathrm{sec}^{-1})$.

the different modes of decomposition of the four dimethylcyclobutanes are neglected then the second-order isomerization rate would be $\frac{1}{4}$ the rate of dimerization of propylene to cyclobutane. Using the same value for the $A$ factor for dimerization of propylene as has been found for the dimerization of tetrafluoroethylene,[9] the activation energy for propylene dimerization is calculated to have the very reasonable value of 30.6 kcal/mole ($E_A$ for dimerization of $C_2F_4$ is 25 kcal/mole). Two of the other dimethylcyclobutanes formed could decompose to ethylene and 2-butene and it is predicted that the ethylene would always contain two D atoms whereas the 2-butene would not contain any. It is not suggested that all the ethylene is formed via this type of reaction. However, the observed high proportion of ethylene-$d_2$ in the products, together with the fact that it appears to be all 1,2-dideuterio- does lend support for the above mechanism for the second-order isomerization reaction. If this explanation is correct, a significant concentration of dimethylcyclobutanes should be formed even though their rate of decomposition at the reaction temperature is fast.[10] At 482°C and a propylene pressure of 100 mm, a stationary-state concentration of approximately 0.6 mm would build up quickly. No mention has been made of cyclobutane products in the high-temperature pyrolyses of propylene.[11] According to the above rate constant the stationary-state concentrations of dimethylcyclobutanes using 100 mm propylene and temperatures of 600° and 700°C would be only $3\times10^{-2}$ and $1.5\times10^{-3}$ mm, respectively. The significance of the reaction in the kinetics could, however, be significantly greater.

There are other possible mechanisms which would explain the increased rate at high pressures. Douglas, Rabinovitch, and Looney[5] found that radicals catalyze the ethylene-$d_2$ isomerization and reaction schemes in-

---

[9] I. M. Butler, J. Am. Chem. Soc. **84**, 1393 (1962).

[10] H. R. Gerberich and W. D. Walters, J. Am. Chem. Soc. **83** 3935 (1961).

[11] A. S. Kallend, J. H. Purnell, and B. C. Shurlock, Proc. Roy. Soc. (London) **A300**, 120 (1967) and references cited therein.

TABLE VI. Arrhenius parameters for the nitric oxide-catalyzed isomerization of simple olefins.

| | $\log A$ (liters mole$^{-1}\cdot$second$^{-1}$) | $E_A$ (kcal mole$^{-1}$) | $\log k_2$(377°C) (liter mole$^{-1}\cdot$second$^{-1}$) | Reference |
|---|---|---|---|---|
| *trans*-$C_2H_2D_2$ | 8.35[a] | 28.4[a] | −1.20 | 12 |
| *cis*-$C_3H_5D$ | 8.27 | 27.9 | −1.11 | This work |
| *cis*-$C_4H_8$ | 7.60 | 26.2 | −1.21 | 1, 13 |

[a] Data quoted by Cundall for this reaction (Ref. 1) is incorrect.

volving radicals may be constructed giving second-order rates of isomerization. These authors considered that dimerization reactions were unimportant because very little ethylene-$d_1$ was found in the pyrolysis of mixtures of $C_2H_4$ and $C_2H_2D_2$. Lack of autocatalysis and reproducibility of rates in the "aged" reaction vessel in the present study suggest that polymerization or other product buildup are not causes of the increased reaction rate at high pressure.

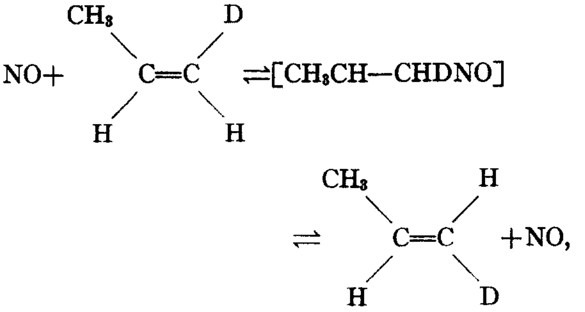
After correction for the heterogeneous and bimolecular [assuming $k_{\text{bimol}}$(liters mole$^{-1}\cdot$second$^{-1}$) $=10^{7.4}\exp(-30\,600/RT)$] reactions, the limiting high-pressure first-order rate constant for isomerization is

$$k_\infty(\text{sec}^{-1})=10^{13.16\pm0.20}\exp[-(61\,300\pm700)/RT].$$

Table V summarizes the high-pressure rate constants for the isomerization of $C_2$ to $C_4$ olefins. It can be seen that the isomerization rate at 500° increases steadily through the series ethylene to 2-butene although activation energies are somewhat scattered. This study does not affect the conclusion reached by Cundall[1] and others that the *cis–trans* isomerization of olefins proceeds via a singlet mechanism. Lin and Laidler[2] have pointed out certain linear energy relationships for olefin isomerizations. Propylene falls reasonably close to the straight lines drawn by them for plots of $E_A$ against heat of hydrogenation and $\Delta H^{\ddagger}$ against $T\Delta S^{\ddagger}$.

### Nitric Oxide-Catalyzed Isomerization

Arrhenius parameters for this reaction are very similar to those measured for dideuterioethylene[12] and 2-butene[13] (Table VI). Values of the rate constants at 650°K show an even more marked similarity. There is obviously almost exact compensation between enthalpy and entropy changes in these reactions. Mechanisms for NO catalysis of *cis–trans* isomerization have recently been summarized.[1] In this instance there seems no reason to use a mechanism other than that originally proposed by Rabinovitch and Looney[12] in which chemical addition of NO to the double bond occurs giving a radical capable of undergoing almost free rotation about this central C–C bond with



subsequent loss of NO. The lifetime of the radical must be short or it must be unreactive otherwise new products resulting from further reaction of this species would be expected.

No explanation can be found for the small positive reaction rate at apparent zero NO pressure. A surface reaction, zero order in NO, is presumably ruled out by the lack of effect of increased surface area on the value of the intercept. Similarly a number of runs made without the addition of NO showed that there was negligible reaction at these temperatures.

---

[12] B. S. Rabinovitch and F. S. Looney, J. Chem. Phys. **23**, 2439 (1955); F. S. Looney, Ph.D. thesis, University of Washington, Seattle, Wash., 1954.

[13] R. B. Cundall and T. F. Palmer, Actes du Deuxieme Congress International de Catalyse, Paris. Editions Technip, 573 (1961).