maximum in Figure 4 is displaced by about 0.7 eV from the band maximum for the photoelectron peak, and in fact the peak at 3,9 eV in Figure 4 might more reasonably be identified with the photoelectron peak at 4.1 eV. It is hoped that further photodissociation studies at higher resolution and sensitivity will resolve this uncertainty and clarify the nature of the primary process in methyl chloride cation photodissociation.

If the photodissociation of cations turns out to proceed commonly *via* the low-lying excited electronic states of the ions, then the icr photodissociation technique may be a precise and convenient indirect method for obtaining optical absorption spectra of cations for levels lying above the dissociation threshold. While the cross-section value obtained for N_2O is probably uncertain within a factor of 2, and that for CH_3Cl is probably $\pm 30\%$, it is still significant that the cross sections for these two processes are different by at least an order of magnitude. This indicates that the cross sections are strongly related to the chemical properties of the ions, and suggests that the systematic study of cation photochemistry will reveal varied and chemically interesting photodissociation patterns for cations.

Acknowledgments. The author wishes to express his appreciation to Mr. Kermit Smyth for his invaluable help and suggestions and for providing the transmission curve of the window, to Professor Bube for the loan of his thermopile, and to Professor John D. Baldeschwieler for his enthusiastic support and encouragement.

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Nitrogen Dioxide Catalyzed Cis–Trans Isomerization of *cis*-2-Butene

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Abstract: Nitrogen dioxide has been found to catalyze the cis–trans isomerization of *cis*-2-butene in the gas phase. At room temperature, for nitrogen dioxide pressures of 0.1–3.0 Torr and *cis*-2-butene pressures of 1.0–30 Torr, the reaction is first order in both reactants and appears to be homogeneous. At room temperature the reaction has a second-order rate constant of 0.148 ± 0.003 l. mol^{-1} sec^{-1}. Over the temperature range 298–338°K, the Arrhenius parameters of the reactions are $\log A$ (l. mol^{-1} sec^{-1}) $= 8.1 \pm 0.2$ and $E_a = 12.1 \pm 0.3$ kcal mol^{-1}. Thermochemical calculations show that these Arrhenius parameters are consistent with a free-radical isomerization mechanism.

Because it is a major pathway for olefin consumption in photochemical smog, photoinitiated oxidation of olefins by NO_2 has been extensively studied.[1] In solution NO_2 is known to react thermally with olefins to form α,β-nitronitrosoalkanes.[2] If this thermal reaction proceeds at a significant rate under atmospheric conditions, it would constitute an important new pathway for atmospheric olefin consumption. Accordingly, we have begun a study of the gas-phase reactions of NO_2 with olefins.

Early in this study we observed that *cis*-2-butene was being isomerized to *trans*-2-butene. Gas-phase thermal cis–trans isomerization of *cis*-2-butene is well known.[3] The reaction has an activation energy of 62.8 kcal mol^{-1}.[4] The isomerization has been shown to be catalyzed by free radicals such as NO,[3a] I,[5] S,[6] HS,[7] and RS.[8] The activation energies of the NO and I catalyzed isomerizations have been measured[3a,5b] and are 26.2 and 9.4 kcal mol^{-1}, respectively.

The ground state of NO_2 has doublet spin multiplicity and, therefore, free-radical character. NO_2 catalyzed cis–trans isomerization of unsaturated fatty acid esters[9] and of poly(*cis*-butadiene) and *cis*-2-butene[10] has been studied in the liquid phase. However, no kinetic data were reported. We here report the results of our gas-phase kinetic study of the NO_2 catalyzed isomerization of *cis*-2-butene to *trans*-2-butene.

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[1] (a) J. J. Bufalini and A. P. Altshuller, *Environ. Sci. Technol.*, 3, 469 (1969); (b) A. P. Altshuller and J. J. Bufalini, *Photochem. Photobiol.*, 4, 97 (1965); (c) R. J. Cvetanović, *J. Air Pollut. Contr. Ass.*, 14, 209 (1964); (d) A. C. Stern, "Air Pollution," 2nd ed, Adademic Press, New York, N. Y., 1968; (e) P. A. Leighton, "Photochemistry of Air Pollution," Academic Press, New York, N. Y., 1961; (f) Air Quality Criteria for Hydrocarbons (AP-64), National Air Pollution Control Administration, Washington, D. C., 1970; (g) Air Quality Criteria for Photochemical Oxidants (AP-63), National Air Pollution Control Administration, Washington, D. C., 1970.

[2] (a) H. Shecter, *Rec. Chem. Progr.*, **25**, 55 (1964); (b) N. W. Cannon, Eastman Organic Chemicals Bulletin, Vol. 42, No. 2, 1970.

[3] (a) R. B. Cundall, *Progr. React. Kinet.*, **2**, 165 (1964); (b) B. S. Rabinovitch and K. W. Michel, *J. Amer. Chem. Soc.*, **81**, 5065 (1959).

[4] S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS 21, U. S. Government Printing Office, Washington, D. C., 1970, p 351.

[5] (a) M. H. Back and R. J. Cvetanović, *Can. J. Chem.*, 41, 1396 (1963); (b) S. W. Benson, K. W. Egger, and D. M. Golden, *J. Amer. Chem. Soc.*, 87, 468 (1965).

[6] M. W. Schmidt and E. K. C. Lee, *J. Chem. Phys.*, **51**, 2024 (1969).

[7] K. Sugimoto, W. Ando, and S. Oae, *Bull. Chem. Soc. Jap.*, **38**, 224 (1965).

[8] D. M. Graham, R. L. Mieville, and C. Sivertz, *Can. J. Chem.*, 42, 2239 (1964).

[9] N. A. Khan, *J. Chem. Phys.*, **23**, 2447 (1955).

[10] I. I. Ermakova, B. A. Dolgoplosk, and E. N. Kropacheva, *Dokl. Akad. Nauk SSSR*, **141**, 1363 (1961).

Experimental Section

Materials. *cis*-2-Butene (Matheson Research grade), *trans*-2-butene (Matheson CP grade), and NO_2 (Baker CP grade) were thoroughly degassed by bulb-to-bulb distillation and then used without further purification. Oxygen (Matheson Research grade) and NO (Baker CP grade) were used as received. Glc analysis showed that the *cis*-2-butene contained less than 0.1% *trans*-2-butene impurity. NO_2, prepared by treating NO with O_2, was used in runs 9–13. Baker NO_2 was used in all other runs. The *trans*-2-butene was used to prepare glc standards.

Apparatus. The all-glass reaction system (total volume 2.65 l.) consisted of a 2.24-l. cell with two exit arms connected by a gas-circulating loop. Gas circulation was produced by a glass paddle wheel housed in the circulating loop and driven by magnetic coupling to an external motor. The reaction system was contained in a simple fiberboard oven (temperature stability ±1°, maximum operating temperature 353°K). The reaction system was serviced by a conventional high-vacuum line. Greaseless O-ring stopcocks were used throughout the reaction system and the high-vacuum line. Pressures were measured using an MKS Baratron gauge (0.01–300 Torr).

Analysis. Direct sampling of the gaseous reaction mixture was accomplished using a Carle microvolume sampling valve (sample loop volume ~170 μl) connected through an O-ring stopcock to the circulating loop of the reaction system. Glc analysis for *cis*- and *trans*-2-butene as a function of time was performed on a 3-ft 100–120 mesh, acid-washed, activated alumina column operated at 353°K. The Varian-Aerograph gas chromatograph was equipped with a flame ionization detector. Peaks were displayed on a 1-mV Leeds and Northrup recorder equipped with a Disc Integrator. The entire analytical system was calibrated using standard gas mixtures prepared using the Baratron gauge. Experiments showed that over the full range of the gas chromatograph, the analytical system was linear in the ratio of the area of the *cis*-2-butene peak to that of *trans*-2-butene. The area ratio of the *cis*- and *trans*-2-butene peaks was also shown to equal the molar ratio of *cis*- and *trans*-2-butene in the gas standards.

Results

For the reaction

$$\textit{cis}\text{-2-butene} \xrightarrow{NO_2} \textit{trans}\text{-2-butene}$$

the initial rate of isomerization *at low conversion* may be written

$$d[T]/dt = k_x[NO_2]_0^m[C]_0^n \quad (1)$$

where k_x is the experimentally determined rate constant, T and C denote *trans*- and *cis*-2-butene, m and n are reaction orders, and the subscript zeros denote initial concentrations. This expression may also be written

$$[T]_t/[C]_0 = k_x[NO_2]_0^m[C]_0^{n-1}t \quad (2)$$

Therefore, a plot of $[T]_t/[C]_0$ *vs.* t, if linear, will have a slope, $S = k_x[NO_2]_0^m[C]_0^{n-1}$. It should be noted that the presence of a *trans*-2-butene impurity in the starting *cis*-2-butene would have no effect on the value of S. Instead, it would produce a nonzero intercept equal to $[T]_0/[C]_0$.

Experimentally, $[T]_t/[C]_t$ was measured as a function of t. Since

$$\frac{[T]_t}{[C]_0} = \frac{[T]_t}{[T]_t + [C]_t} = \frac{1}{1 + ([C]_t/[T]_t)} \quad (3)$$

the dependence of $[T]_t/[C]_0$ on t could be determined. All experiments were carried out to conversions lower than 5%. As expected for such low conversions, the observed dependence was linear. Table I presents our experimental results. Values of S were obtained by a least-squares treatment.[11] Values of k_x were calculated as described below.

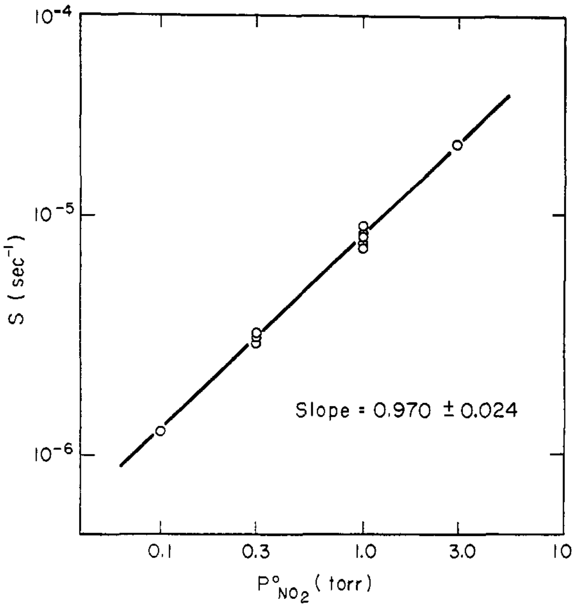

Figure 1. Reaction order with respect to NO_2 for the NO_2 catalyzed isomerization of *cis*-2-butene. Log–log plot of S *vs.* $P_{NO_2}{}^0$.

Reaction Orders. Figure 1 presents a plot of log S *vs.* log $[NO_2]_0$. The slope of the linear correlation is 0.969 ± 0.024.[12] Therefore, $m = 1$. Figure 2 presents a plot of log $[S([C]_0/[NO_2]_0)]$ *vs.* log $[C]_0$. The slope of the linear correlation is 0.983 ± 0.018. Therefore, $n = 1$ and over the NO_2 pressure range, 0.1–3.0 Torr, and the *cis*-2-butene pressure range, 1.0–30 Torr, the overall rate equation can be written as

$$d[T]/dt = k_x[NO_2]_0[C]_0 \quad (4)$$

Table I. Kinetic Data for the NO_2 Catalyzed Cis–Trans Isomerization of *cis*-2-Butene

Run	$P_C{}^0$, Torr	$P_{NO_2}{}^{0,c}$ Torr	Temp, °K	$(S) \times 10^6$ sec^{-1}	$S[C]_0/[NO_2]_0 \times 10^4$ sec^{-1}	k_x, l. mol^{-1} sec^{-1}
1	30.0	0.100	298	0.833	2.50	0.155
2	30.0	0.300	298	2.57	2.57	0.159
3	30.0	1.00	298	6.95	2.08	0.129
4	30.0	3.00	298	22.9	2.28	0.141
5	1.00	1.00	298	8.80	0.0880	0.163
6	3.00	1.00	298	8.22	0.247	0.153
7	10.0	1.00	298	7.28	0.727	0.135
8[a]	1.00	1.00	298	7.76	0.0775	0.144
9[a]	10.0	0.300	298	2.35	0.789	0.147
10[b]	10.0	0.300	298	2.43	0.806	0.150
				$k_x(298\,°K) = 0.148 \pm 0.003$		
11[b]	10.0	0.300	317	6.94	2.30	0.458
12[b]	10.0	0.300	330	14.6	4.84	1.00
13[b]	10.0	0.100	338	8.66	8.66	1.83

[a] Cell packed with glass beads. [b] NO_2 prepared by the reaction $2NO + O_2 \rightarrow 2NO_2$. [c] Using data from the JANAF thermochemical tables, the amount of N_2O_4 present in 3.0 Torr of NO_2 may be calculated to be 2.7% and the amount of N_2O_4 in 1.0 Torr of NO_2 to be less than 1%. Therefore, the measured pressures of NO_2 are not corrected to take account of the equilibrium $2NO_2 \rightleftarrows N_2O_4$.

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(11) All linear correlations including those displayed graphically were obtained by a least-squares treatment.

(12) All error limits cited in this paper are one σ standard deviation.

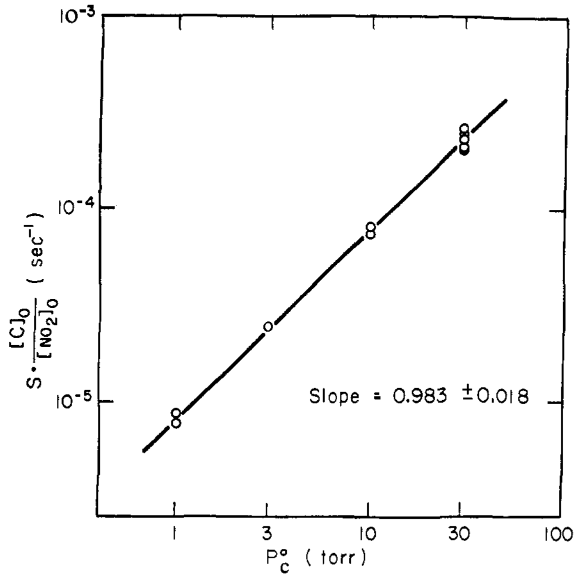


Figure 2. Reaction order with respect to *cis*-2-butene for the NO_2 catalyzed isomerization of *cis*-2-butene. Log-log plot of $S([C]_0/[NO_2]_0)$ *vs.* $P_C{}^0$.

Accordingly, the second-order rate constant k_x is given by $k_x = S/[NO_2]_0$. The values of k_x listed in Table I were calculated in this manner. The ten room-temperature experiments have an average value of $k_x = 0.148 \pm 0.003$ l. mol^{-1} sec^{-1}.

Arrhenius Parameters. Figure 3 presents a plot of log k_x *vs.* $1/T$. The line is the least-squares line calculated using all of the data presented in Table I. From the slope and intercept of the line, the Arrhenius parameters for this reaction were determined to be log A_x (l. mol^{-1} sec^{-1}) = 8.07 ± 0.23 and E_x = 12.14 ± 0.33 kcal mol^{-1}. Because of the limited temperature range and small number of experiments of this temperature study, these computed error limits are probably fortuitously small.

Control Experiments. In order to determine the importance of surface effects and of impurities in the NO_2, several control experiments were performed. Without NO_2 no isomerization occurred. With NO instead of NO_2 no isomerization occurred. A 6.5-fold increase in the ratio of reaction system surface area to reaction system volume (the reaction cell was packed with glass beads) produced a negligible decrease in k_x (runs 8 and 9). Use of NO_2 produced by reacting NO with O_2 gave no significant change in k_x (run 10). These results show that the NO_2 catalyzed isomerization is essentially homogeneous and that no significant contribution to the rate of the reaction was made by any NO impurity.

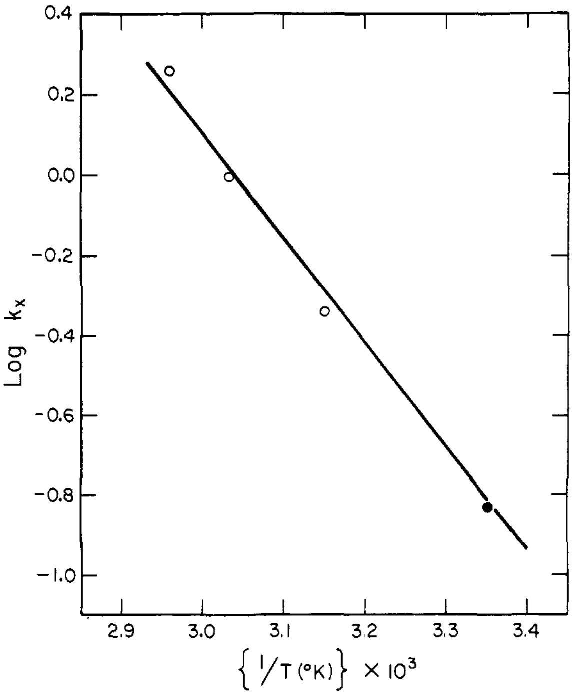
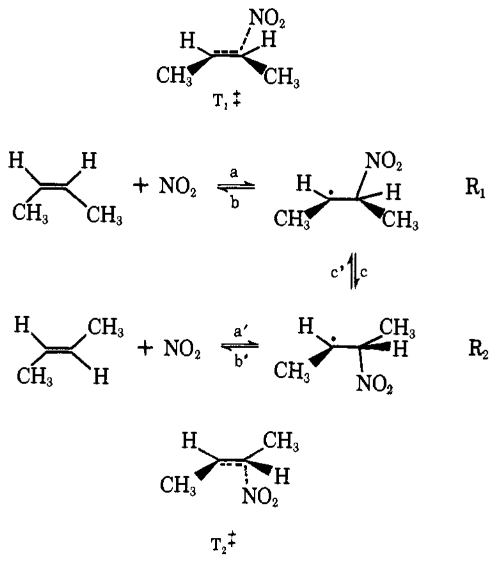


Figure 3. Arrhenius parameters for the NO_2 catalyzed isomerization of *cis*-2-butene. Plot of log k_x *vs.* the reciprocal of *T*. The solid point is the average value of k_x for the ten room-temperature runs.



(5)

Discussion

By analogy to the mechanisms proposed in the previous studies[5] of free-radical catalyzed cis–trans isomerizations of olefins, the mechanism of the NO_2 catalyzed cis–trans isomerization of *cis*-2-butene is most likely that shown in eq 5. Assuming that the radical intermediates, R_1 and R_2, reach a steady state, the following expression, describing the rate of disappearance of *cis*-2-butene, can be derived

$$-\frac{d[C]}{dt} = \left\{\frac{K_{ab}k_c}{1 + K_{cb} + K_{c'b'}}\right\} \times [NO_2]_0\left\{[C]_0 - \left[1 + \frac{K_{a'b'}k_{c'}}{K_{ab}k_c}\right][T]\right\} \quad (6)$$

where $K_{ij} = k_i/k_j$. For low conversions, where $[T] \ll [C]_0$, this expression reduces to

$$-\frac{d[C]}{dt} = \frac{d[T]}{dt} = \left\{\frac{K_{ab}k_c}{1 + K_{cb} + K_{c'b'}}\right\}[NO_2]_0[C]_0 \quad (7)$$

Comparison of eq 7 and 4 shows that

$$k_x = K_{ab}k_c/(1 + K_{cb} + K_{c'b'}) \quad (8)$$

If k_a, k_b, and k_c can be calculated and if the relative magnitudes of K_{cb} and $K_{c'b'}$ can be estimated, then substitution in (8) will permit a value of k_x to be calculated. Reasonable agreement of this calculated value of k_x

with the experimental value would provide significant support for the proposed mechanism (5). From thermochemical data the heat of reaction of step a, $\Delta H_{ab}{}^{\circ,c}$, can be calculated (see Appendix A) to be exothermic by 2.8 ± 1 kcal mol^{-1}. By comparison to other bond-rotation reactions,[5b,13,14] the activation energy of step c, E_c, can be estimated (see Appendix B) to be ~4 kcal mol^{-1}. Therefore, the transition state ($T_R{}^{\ddagger}$) for bond rotation in the radicals R_1 and R_2 must have essentially the same energy as the initial system (NO_2 + *cis*-2-butene). This means that the observed activation barrier of 12.1 kcal mol^{-1} must correspond to the height of either $T_1{}^{\ddagger}$ or $T_2{}^{\ddagger}$, the transition states for NO_2 addition to *cis*- and *trans*-2-butene. Actually, $T_1{}^{\ddagger}$ and $T_2{}^{\ddagger}$ should be nearly identical energetically, differing primarily because of the repulsion of the two methyl groups in the cis transition state $T_1{}^{\ddagger}$. A good estimate of the size of this repulsion is 0.4 kcal mol^{-1}, the difference between the heats of formation of *cis*- and *trans*-2-butene. Therefore, $E(T_1{}^{\ddagger}) \approx E(T_2{}^{\ddagger}) + 0.4$, which means that $E_a = E(T_1{}^{\ddagger}) \approx E_x = 12.2$ kcal mol^{-1}. Since $E_b = E_a - \Delta H_{ab}{}^{\circ,c}$, $E_b \approx 15.0$ kcal mol^{-1}.

Reasonable estimates (see Appendix B) for A_b and k_c are $A_b = 10^{13.6}$ sec^{-1} and $k_c = 10^{11.4}10^{-4.3/\theta}$ sec^{-1}, where $\theta = 2.3RT$. Therefore, $k_b = 10^{13.6}10^{-15.0/\theta}$ sec^{-1}, and at 300°K K_{cb} is given by $K_{cb} = k_c/k_b = 10^{5.6} \gg 1$, which means that in the radical R_1 bond rotation (step c) is much faster than bond breaking (step b). Therefore, NO_2 addition to the double bond (step a) is the rate-determining step of the overall reaction.

Because K_{cb} is so large, eq 8 may be simplified and rearranged to give

$$k_x = \frac{k_a}{1 + \dfrac{K_{c'b'}}{K_{cb}}}$$

where

$$\frac{K_{c'b'}}{K_{cb}} = \frac{A_{c'}A_{b'}}{A_cA_b}e^{(E_c + E_b - E_{c'} - E_{b'})/RT} \tag{9}$$

But the radicals R_1 and R_2, like the transition states $T_1{}^{\ddagger}$ and $T_2{}^{\ddagger}$, should differ energetically only by about 0.4 kcal mol^{-1}, R_1 being higher in energy than R_2, because of the cis methyl–methyl repulsion. This means that $E_{c'} \approx E_c + 0.4$. Since $E(T_1{}^{\ddagger}) \approx E(T_2{}^{\ddagger}) + 0.4$, $E_b \approx E_{b'}$. Therefore, since the quotient of the A factors should be very close to unity, $K_{c'b'}/K_{cb} \approx e^{-0.4/RT}$. Over the temperature range of our experiments (298–338°K), the exponent $(-0.4/RT)$ varies only slightly (−0.67 to −0.55). Thus, $1 + K_{c'b'}/K_{cb} \approx 10^{0.2}$ and k_x can be written as

$$k_x \approx k_a/10^{0.2} \tag{10}$$

Knowing $\Delta S_{ab}{}^{\circ,c}$ and having estimated A_b permits A_a to be estimated as $10^{7.8}$ l. mol^{-1} sec^{-1} (see Appendix B). Substituting in eq 10, one obtains a calculated value of $A_x{}^{calcd} = 10^{7.6}$ l. mol^{-1} sec^{-1} for the frequency factor of the overall reaction rate constant k_x. Comparison of this value with the experimental frequency factor of $A^{exptl} = 10^{8.1 \pm 0.2}$ l. mol^{-1} sec^{-1} shows that they agree to within a factor of 2, which is quite acceptable considering the accuracy of the temperature study. Equation 10 also confirms the previously stated qualitative conclusion that the experimentally observed activation energy E_x should equal the activation energy of the radical-forming step a. For such an addition reaction the observed activation energy of 12.1 kcal mol^{-1} is quite reasonable.

It is worthwhile to compare the present results obtained for NO_2 catalyzed isomerization, where the addition step is rate determining, to those obtained for NO and I catalyzed isomerization, where bond rotation is rate determining.[5b] The change in the rate-determining step from bond rotation to catalyst addition is easily understood, since for NO and I the catalyst addition step is endothermic by 19 and 5 kcal mol^{-1}, respectively,[5b] while for NO_2, it is exothermic by 2.8 kcal mol^{-1}. This difference results largely from the difference in the bond strengths of the C–NO_2, C–NO, and C–I bonds in the intermediate radical R_1. Thus $D(C\text{–}NO_2) = 60$ kcal mol^{-1} (see Appendix A), which is 2.2 kcal mol^{-1} larger than the π-bond energy of *cis*-2-butene (57.8 kcal mol^{-1}). In contrast to this, $D(C\text{–}NO) = 37$ kcal mol^{-1} and $D(C\text{–}I) = 51$ kcal mol^{-1},[5b] both smaller than the π-bond energy of *cis*-2-butene (see Appendix A). The exothermicity of the NO_2 addition step makes $K_{cb} \gg 1$ for NO_2, and therefore the addition step is rate determining. The endothermicity of the NO and I addition steps makes $K_{cb} \ll 1$, and therefore the bond-rotation step is rate determining.

Because $K_{cb} \gg 1$ for NO_2, the intermediate radicals R_1 and R_2 should be relatively long-lived, facilitating further reaction of the radicals to form molecular double addition products. Presumably, this accounts for the facile reaction in solution at room temperature of NO_2 with olefins to give mixtures of α,β-dinitro- and α,β-nitronitrosoalkanes.[2] In the gas phase these addition reactions are unstudied. However, Cottrell and Graham[15] have studied the gas-phase thermal oxidation of ethylene and propylene by NO_2 at elevated temperatures where the initial double addition products are thermally decomposed. They suggest that the rate-controlling step for NO_2 consumption is the initial addition step of NO_2 to the olefin double bond. Extrapolation of their data for propylene to room temperature and comparison with our isomerization results shows that *cis*-2-butene consumption by NO_2 should be competitive with NO_2 catalyzed cis–trans isomerization only when NO_2 pressures are greater than 1000 Torr. Clearly, for our experimental conditions ($P_{NO_2} \leqq 3.0$ Torr) no olefin consumption should have occurred and, as was the case, total pressure should have remained constant throughout any isomerization run.

If formed in a polluted atmosphere the radicals R_1 and R_2 should be readily captured by oxygen to give a nitroalkylperoxy radical. Conversion of this radical to stable products would represent a nonphotolytic pathway for atmospheric olefin oxidation and could be highly significant for olefin consumption in smog. We are presently investigating the reactions of NO_2 with olefins in the presence of oxygen.

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(13) J. Dale, *Tetrahedron*, **22**, 3373 (1966).

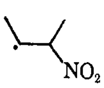
(14) Reference 4, p 54.

(15) (a) T. L. Cottrell and T. E. Graham, *J. Chem. Soc.*, 556 (1953); (b) *ibid.*, 3644 (1954).

Public Health Service, and by Themis Grant No. NO0014-69-A-0200-500. One of us (J. L. S.) acknowledges an Air Pollution Special Postdoctoral Fellowship.

Appendix A[16]

Calculation of $\Delta H_{ab}°$. $\Delta H_{ab}°$ may be calculated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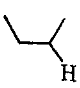
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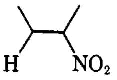
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from the data presented in Table II in at least two ways,

$$\Delta H_{ab}° = \Delta H_f°(\mathbf{1}) - \Delta H_f°(\mathbf{2}) - \Delta H_f°(NO_2) \quad (A1)$$

and

$$\Delta H_{ab}° = D_\pi(\mathbf{2}) - D_{C-NO_2}(\mathbf{1}) \quad (A2)$$

$\Delta H_f°(\mathbf{1})$, $D_\pi(\mathbf{2})$, and $D_{C-NO_2}(\mathbf{1})$ are not directly available and must be calculated.

$$\Delta H_f°(\mathbf{1}) = \Delta H_f°(\mathbf{4}) - \Delta H_f°(H\cdot) + D_{C-H}(\mathbf{4}) \quad (A3)$$

Taking the value of $D_{C-H}(\mathbf{3})$ to be 95.3 kcal mol^{-1} [17] as a model for $D_{C-H}(\mathbf{4})$ permits calculation of $\Delta H_{ab}°$ by method A1. Appropriate substitution in (A1) and use of the values in Table II yields $\Delta H_{ab}° = -2.1$ kcal mol^{-1}.

$$D_\pi(\mathbf{2}) = 2D_{C-H}(\mathbf{3}) - D_{H-H}(H_2) - \Delta H°_{\text{hydrogenation}}(\mathbf{2}) \quad (A4)$$

where $H°_{\text{hydrogenation}}(\mathbf{2}) = 28.6$ kcal mol^{-1} [18] and $D_{H-H}(H_2) = 104.2$ kcal mol^{-1}.[19] Substituting in (A4) one obtains $D_\pi(\mathbf{2}) = 57.8$ kcal mol^{-1}.

$$D_{C-NO_2}(\mathbf{4}) = \Delta H_f°(\mathbf{5}) + \Delta H_f°(NO_2) - \Delta H_f°(\mathbf{4}) \quad (A5)$$

Taking $D_{C-NO_2}(\mathbf{1})$ to be equal to $D_{C-NO_2}(\mathbf{4})$ and substituting values from Table II gives $D_{C-NO_2}(\mathbf{1}) = 60.0$ kcal mol^{-1}, and now $\Delta H_{ab}°$ may be calculated by substitution in (A2) to be -2.2 kcal mol^{-1}. Comparing the two values (-2.1 and -2.2 kcal mol^{-1}) gives $\Delta H_{ab}° = -2.2 \pm 1$ kcal mol^{-1} as a reasonable result. In concentration units this becomes $\Delta H_{ab}°{}^{,c} = -2.8 \pm 1$ kcal mol^{-1}.

Calculation of $\Delta S_{ab}°$.

$$\Delta S_{ab}° = S°(\mathbf{1}) - S°(\mathbf{2}) - S°(NO_2) \quad (A6)$$

Table II. Thermochemical Data for the Calculation of $\Delta H_{ab}°$ and $\Delta S_{ab}°$

Species	$\Delta H_f°$, kcal mol^{-1}	$S°$, eu
2	-1.7^a	72.10^a
NO_2	7.9^a	57.3^a
4	-39.1^b	
H	52.1^a	
5	13.0^c	

[a] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 23. [b] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 69, 279 (1969). [c] Reference 17.

where $S°(\mathbf{2}) = 72.1$ and $S°(NO_2) = 57.3$ eu (see Table II). Data sufficient for the calculation of $S°(\mathbf{1})$ is lacking. Instead, $S°(\mathbf{1})$ must be estimated using Benson's additivity rules for group properties.[20,21] Thus

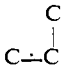
$$S°(\mathbf{1}) = S°(\mathbf{4}) + R \ln 2 \text{ (spin correction)}$$

$$S°(\mathbf{4}) = 2S°[C\text{-}(H)_3(C)_1] + S°[C\text{-}(H)_2(C)_2] + S°[C\text{-}(H)_1(C)_2(NO_2)_1] - 2R \ln 3(CH_3 \text{ sym}) - R \ln 2(NO_2 \text{ sym}) + R \ln 2(\text{mixing optical isomers}) = 92.8 \text{ eu} \quad (A7)$$

Therefore, $S°(\mathbf{1}) = 94.2$ eu and $\Delta S_{ab}° = -35.2$ eu. In concentration units this becomes $\Delta S_{ab}°{}^{,c} = -26.8$ eu.

Appendix B

Estimation of A_b and A_a. $\Delta S_b^{\ddagger}$ can be estimated by estimating the changes in rotational and vibrational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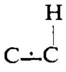
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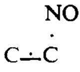
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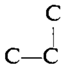
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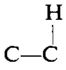
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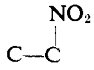
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entropy in the radical, R_1, on passing to the transition state, $T_1^{\ddagger}$. Using the methods and terminology of Benson and O'Neal,[22] $\Delta S_b^{\ddagger}$ can be calculated as follows.

$$\Delta S_b^{\ddagger} = S°[(C\text{–}NO_2)_{rc} + (C\dot{-}C)_s^{1300} + (C\text{–}C)_t^{110} + 2(\mathbf{6})_b^{400} + 2(\mathbf{7})_b^{800} + (\mathbf{8})_b^{200} + 2(NO_2)^{160}{}_{1e\ \text{rock}}] - S°[(C\text{–}NO_2)_s^{900} + (C\text{–}C)_s^{1000} + (\mathbf{9})_4 + 2(\mathbf{10})_b^{350} + 2(\mathbf{11})^{1150} + (\mathbf{12})_b^{400} + 2(NO_2)^{550}{}_{2e\ \text{rock}}] = [0.0 + 0.0 + 3.3 + 2(1.0) + 2(0.2) + 2.2 + 2(2.7)] - [0.2 + 0.1 + 6.4 + 2(1.2) + 2(0.05) + 1.0 + 2(0.6)] \quad (B1)$$

Therefore, $\Delta S_b^{\ddagger} = 1.9$ eu and $A_b = (ekT/h)e^{\Delta S_b^{\ddagger}/R} = 10^{13.6}$. Because this calculation neglects rotational entropy, which should increase with stretching of the C-NO_2 bond, the value of 1.9 eu for $\Delta S_b^{\ddagger}$ is probably slightly too low. This conclusion is further supported by the observation that most molecular fission processes have A factors[23] in the range 10^{14}–10^{17} sec^{-1}. Having estimated A_b, A_a can now be calculated. Thus, $A_a/A_b = e^{\Delta S_{ab}°{}^{,c}/R}$ and $A_a = 10^{7.8}$ l. mol^{-1} sec^{-1}.

Estimation of k_c.

$$k_c = (kT/h)K_c^{\ddagger}e^{-E_c/RT} \quad (B2)$$

The partition function for the rotational transition state should differ significantly from that of the radical R_1 only in that it lacks the partition function describing motion along the reaction coordinate. Thus, $(K_c^{\ddagger})^{-1} \approx Q_R = [8\pi^3IkT/h^2]^{1/2}$, where Q_R is the partition function for bond rotation in the radical R_1. The moment of inertia, I, for rotation of an ethylidene group about a C-C bond is calculated to be 43.3 amu Å^2, assuming that the -CH(CH_3)(NO_2) group is an infinite

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[16] Values of $\Delta H°$ and $\Delta S°$ are referred to 298°K and 1 atm; values of $\Delta H°{}^{,c}$ and $\Delta S°{}^{,c}$ are referred to 298°K and 1 M.

[17] D. M. Golden and S. W. Benson, *Chem. Rev.*, 69, 125 (1969).

[18] R. T. Morrison and R. N. Boyd, "Organic Chemistry," Allyn and Bacon, Boston, Mass., 1966, p 181.

[19] B. deB. Darwent, "Bond Dissociation Energies in Simple Molecules," NSRDS-NBS 31, U. S. Government Printing Office, Washington, D. C., 1970, p 32.

[20] (a) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 23; (b) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 69, 279 (1969).

[21] Reference 4, pp 1–62.

[22] Reference 4, p 39.

[23] Reference 20a, p 70.

mass. Substituting, one obtains

$$k_c = [k/8\pi^3 I]^{1/2} T^{1/2} e^{-E_c/RT} \qquad \text{(B3)}$$

In Arrhenius form ($T = 300°K$) this becomes

$$k_c = [k/8\pi^3 I]^{1/2} 10^{1.5} 10^{-(E_c + 0.3)/\theta} \qquad \text{(B4)}$$

where $[k/8\pi^3 I]^{1/2} 10^{1.5} = A_c$. E_c should be similar to the rotation barrier[5b,13,14] of the analogous nitroso radical **1**. Therefore, $E_c \approx 4 \pm 0.5$ kcal mol^{-1} and, after appropriate substitution in (B3), one obtains $k_c = 10^{11.4} 10^{-4.3/\theta}$ sec^{-1}.

Enthalpies of Formation for Globular Molecules. III. Succinonitrile and Triethylenediamine[1]

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Abstract: Enthalpies of combustion have been measured for crystalline succinonitrile and 1,4-diazabicyclo[2.2.2]-octane, and the derived enthalpies of formation at 298.15°K in the crystalline state, $\Delta H_f°(c)$, are 33.38 ± 0.16 and 6.75 ± 0.96 kcal/mol, respectively. Adjuvant data for both compounds permit evaluation at 298.15°K of the corresponding enthalpy values, $\Delta H_f°(g)$, for the gaseous compounds as 50.11 ± 0.16 and 21.6 ± 1.6 kcal/mol. The strain energies of the compounds are discussed.

Two interesting, nitrogen-containing plastically crystalline substances, which already have been studied by thermophysical methods over an extended range of temperature, are here examined by thermochemical means. Although data for succinonitrile[3] and for 1,4-diazabicyclo[2.2.2]octane[4] (triethylenediamine) do exist in the literature, that on the former did not appear to be a definitive value and that on the latter led to an interpretation of strain energies clearly at variance with those observed for homologous bicyclo compounds.[5]

Experimental Section

Preparation, purification, and characterization details of the calorimetric samples as 99.93% pure succinonitrile[6,7] and 99.7% pure triethylenediamine,[8,9] the constructional features and operational procedures of the rotating-bomb calorimeter, and reduction of data[10] have been described elsewhere. The standard symbolism has been retained here.[11] Calibration of the calorimeter with NBS standard benzoic acid sample 39i[12] for these compounds yielded $\mathcal{E}°(\text{calor}) = 3969.63 \pm 0.10$ cal °K^{-1} for the determinations on succinonitrile, 3973.44 ± 0.06 cal °K^{-1} for those on the diamine. To protect both substances from CO_2 and H_2O (triethylenediamine is especially sensitive and fairly volatile also), the pellets were loaded into Type A DuPont Mylar (polyester) bags. The $\Delta E_c°/M$ for this sample of Mylar was determined in a separate series of experiments to be $-5479.30 + (0.2524RH)$ cal/g. Here, RH is the relative humidity expressed in per cent. The ΔE_c of the cotton fuse was -4108 cal g^{-1}. A deep, platinum crucible was used for combustions of both substances; a platinum baffle was found advantageous to avoid soot during combustion of the diamine.

All values are given in defined thermochemical calories equal to 4.1840 J; 1961 atomic weights are used and the ice point is taken as 273.15°K. The values of the parameters used for converting the measured quantities to weights *in vacuo*, to the isothermal process, and to standard states are given in Table I. These values were obtained from the literature. Those in parentheses were estimated by analogy with those of similar materials. Contributory enthalpies of formation, $\Delta H_f°$, were taken from ref 13. They are -94.051 kcal mol^{-1} for carbon dioxide (g) and -68.315 kcal mol^{-1} for water (l).

Table I.

Substance	Density, g cm^{-3}	C_p, cal (g °K)$^{-1}$	$(\partial V/\partial T)_p$, l. g^{-1} °K^{-1}
Succinonitrile	1.04	0.4345	(0.52 × 10^{-6})
Triethylenediamine	1.147	0.3255	(0.52 × 10^{-6})
Mylar	1.38	0.315	(0.111 × 10^{-6})

Results

Calorimetric Results. Seven combustions were made of succinonitrile and six of triethylenediamine. Data from combustions selected as typical for each compound are summarized in Table II. The results of the individual combustion experiments in terms of $-\Delta E_c°/M$ at 298.15°K are summarized in Table III and refer to the following reaction

$$C_4H_4N_2(c) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l) + N_2(g)$$

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[2] To whom correspondence concerning this paper should be directed.

[3] M. S. Kharasch, *J. Res. Nat. Bur. Stand.*, **2**, 359 (1929).

[4] M. Parris, P. S. Raybin, and L. C. Labowitz, *J. Chem. Eng. Data*, **9**, 221 (1964).

[5] S.-W. Wong and E. F. Westrum, Jr., *J. Amer. Chem. Soc.*, in press.

[6] C. A. Wulff and E. F. Westrum, Jr., *J. Phys. Chem.*, **67**, 2376 (1963).

[7] E. F. Westrum, Jr., *J. Chim. Phys. Physicochim. Biol.*, **63**, 52 1966).

[8] S. S. Chang and E. F. Westrum, Jr., *J. Phys. Chem.*, **64**, 1551 (1960).

[9] J. C. Trowbridge and E. F. Westrum, Jr., *ibid.*, **67**, 2381 (1963).

[10] M. Månsson, N. Rapport, and E. F. Westrum, Jr., *J. Amer. Chem. Soc.*, **92**, 7296 (1970).

[11] W. N. Hubbard, D. W. Scott, and G. Waddington in "Experimental Thermochemistry," Interscience, New York, N. Y., 1956.

[12] K. L. Churney and G. T. Armstrong, *J. Res. Nat. Bur. Stand., Sect. A*, **72**, 453 (1968).

[13] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note 270-3, Jan 1968.