

Nitrogen Dioxide Catalyzed Geometric Isomerization of Olefins. Isomerization Kinetics of the 2-Butenes and the 2-Pentenes

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Abstract: Arrhenius parameters have been determined for the NO₂ catalyzed geometric isomerization of the 2-butenes and the 2-pentenes. For *cis*-2-butene, *trans*-2-butene, *cis*-2-pentene, and *trans*-2-pentene respectively E , kcal mol⁻¹ = 11.8, 12.2, 11.2, and 12.5 and log A , l. mol⁻¹ sec⁻¹ = 7.86, 7.65, 7.49, and 7.72 over the temperature ranges 298–366, 297–370, 298–381, and 298–382°K. Combination of these results with the results of thermochemical calculations permits calculation of 298°K rate constants for NO₂ addition to the double bond of ten simple olefins. These rate constants suggest that this reaction is unimportant in the bulk consumption of atmospheric olefin pollutants.

Previously we reported that NO₂ catalyzes the thermal geometric isomerization of the 2-butenes and the 2-pentenes.² By analogy to previous studies of radical catalyzed geometric olefin isomerizations,³ we suggested that the isomerization proceeded by NO₂ addition to the olefin double bond to form a nitroalkyl radical, followed by bond rotation and loss of NO₂ to form the isomeric olefin.^{2a} We also noted that in a polluted urban atmosphere capture of the intermediate nitroalkyl radical by molecular oxygen would constitute a thermal pathway for the atmospheric oxidation of olefin pollutants which, if fast enough, could be of considerable significance for the formation of smog. In this paper we described the results of detailed studies of the kinetics of geometric isomerization of the 2-butenes and the 2-pentenes and the use of these results to estimate the importance for the consumption of atmospheric olefin pollutants of processes initiated by NO₂ addition to an olefin double bond.

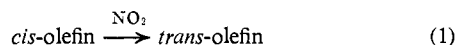
Experimental Section

The chemicals, apparatus, and analytical methods used in this study have been described in two previous papers.²

Results

The equations used to develop the experimental data were identical for all four olefins. They will be described only as they apply to *cis*-olefin. Exchanging the symbols C and T will yield the corresponding equations for *trans*-olefin.

For the reaction



the initial rate of isomerization at low conversion may be written^{2a}

$$d[\text{T}]/dt = k_{\text{cis}}[\text{NO}_2]_0[\text{C}]_0 \quad (2)$$

where k_{cis} is the experimentally determined rate constant, T and C denote *trans*- and *cis*-olefin and the zero

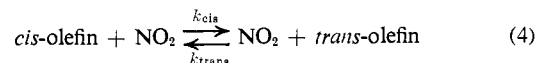
subscripts denote initial concentrations. This expression may also be written

$$[\text{T}]_t/[\text{C}]_0 = k_{\text{cis}}[\text{NO}_2]_0 t \quad (3)$$

Since $[\text{T}]_t/[\text{C}]_0 = (1 + [\text{C}]_t/[\text{T}]_t)^{-1}$ by measuring $[\text{C}]_t/[\text{T}]_t$ as a function of time (t), the observed rate constant, k_{cis} , can be determined easily and precisely.

All experiments were run to conversions of less than 5%. As expected for such low conversions, the observed dependence of $[\text{C}]_t/[\text{T}]_t$ on t was always linear. Figure 1 illustrates the precision of the linearity routinely obtained. Nevertheless, this apparent linearity must mask the perturbing effects of some reverse isomerization.

Normal kinetic treatment of the following reaction scheme



yields eq 5, where $K_{\text{TC}} = k_{\text{trans}}/k_{\text{cis}}$. Iterative use of

$$k_{\text{cis}} t = -\frac{1}{[1 + K_{\text{TC}}][\text{NO}_2]_0} \times \ln \left\{ 1 - [1 + K_{\text{TC}}] \frac{[\text{T}]_t}{[\text{C}]_0 + [\text{T}]_0} \right\} \quad (5)$$

eq 5 allowed the raw rate constants (k_{cis} or k_{trans}) calculated using eq 3 to be corrected for the perturbing effects of reverse isomerization. To do this the raw values for k_{cis} and k_{trans} were used to calculate an initial set of Arrhenius parameters for these rate constants. An initial value of K_{TC} (or K_{CT}) was then calculated from these Arrhenius parameters. Substitution of this value into eq 5 now allowed a new set of values for k_{cis} (or k_{trans}) to be calculated. This process was repeated until a consistent set of values was obtained for k_{cis} and k_{trans} . These values and our experimental conditions are tabulated in a supplemental table presented in the microfilm edition of this journal.

Arrhenius Parameters

Figures 2 and 3 present plots of $\log k$ vs. θ^{-1} where $\theta = 2.3RT$. The lines are the least-squares lines calculated from the data presented in the microfilm edition.

(1) National Institute for Environment, Yatabe, Ibaraki, Japan.

(2) (a) J. L. Sprung, H. Akimoto, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **93**, 4358 (1971); (b) H. Akimoto, J. L. Sprung, and J. N. Pitts, Jr., *ibid.*, **94**, 4850 (1972).

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

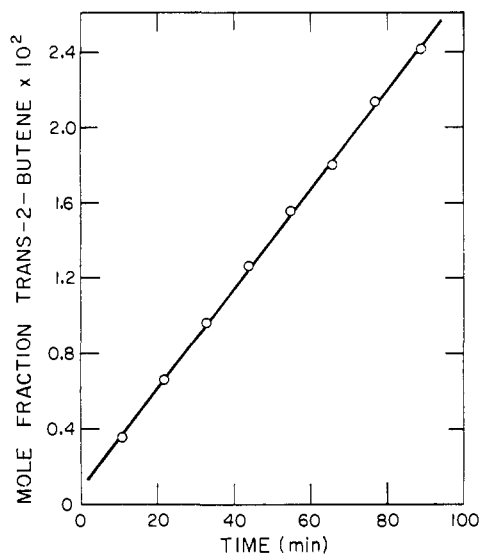


Figure 1. Plot of the mole fraction of *trans*-2-butene vs. time for the *cis*- to *trans*-NO₂ catalyzed geometric isomerization of *cis*-2-butene. The least-squares slope of the plot is $2.64 \pm 0.03 \times 10^{-4} \text{ min}^{-1}$. Reaction conditions were 9.00 Torr of *cis*-2-butene, 0.100 Torr of NO₂, and $54.4 \pm 0.2^\circ$. The nonzero intercept is due to the presence of a trace of *trans*-2-butene impurity in the starting *cis*-2-butene.

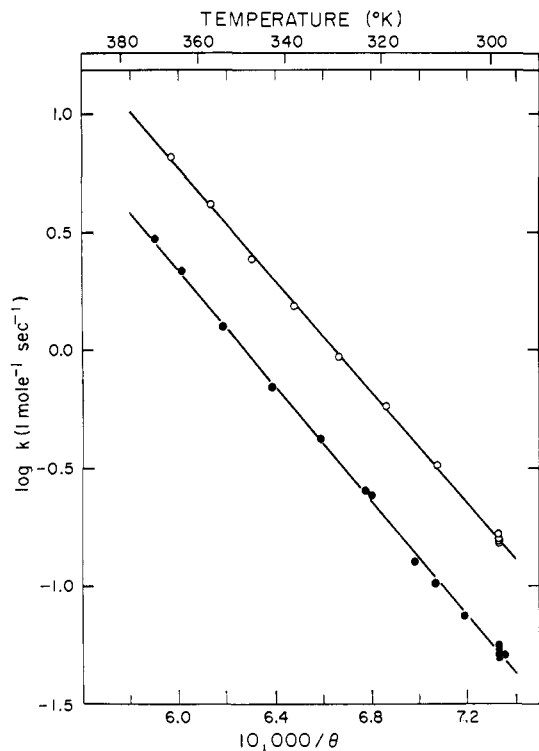


Figure 2. Arrhenius parameters for the NO₂ catalyzed geometric isomerization of *cis*- or *trans*-2-butene. Plot of $\log k$ vs. θ^{-1} where $\theta = 2.3RT$: (○) *cis*-2-butene; (●) *trans*-2-butene.

The slope and intercept of each least-squares line give the Arrhenius parameters of that reaction. Table I

Table I. Arrhenius Parameters for the NO₂ Catalyzed Geometric Isomerization of the 2-Butenes and the 2-Pentenes

Olefin	E , kcal mol ⁻¹	Log A , l. mol ⁻¹ sec ⁻¹
<i>cis</i> -2-Butene	11.81 ± 0.083	7.861 ± 0.058
<i>trans</i> -2-Butene	12.19 ± 0.118	7.652 ± 0.081
<i>cis</i> -2-Pentene	11.23 ± 0.092	7.494 ± 0.062
<i>trans</i> -2-Pentene	12.48 ± 0.088	7.720 ± 0.059

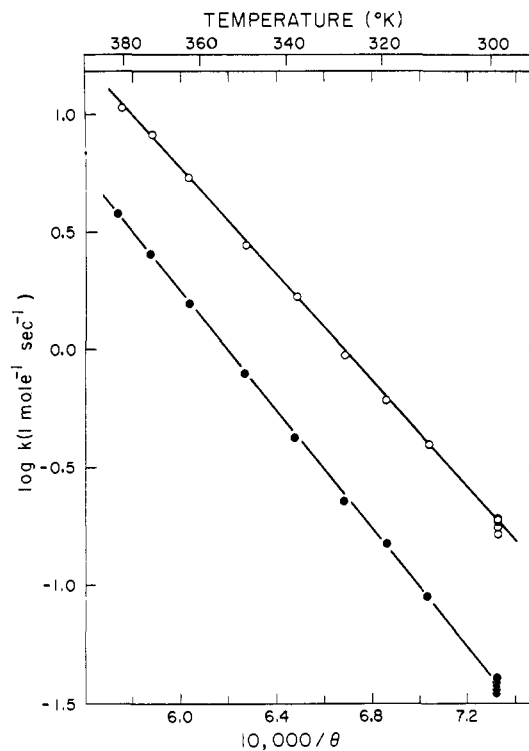


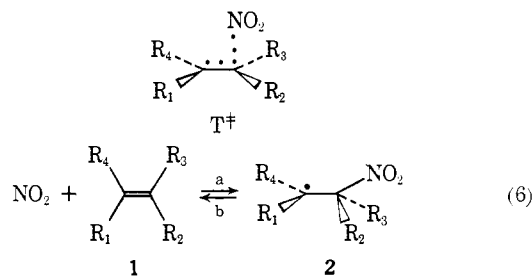
Figure 3. Arrhenius parameters for the NO₂ catalyzed geometric isomerization of *cis*- or *trans*-2-pentene. Plot of $\log k$ vs. θ^{-1} where $\theta = 2.3RT$: (○) *cis*-2-pentene; (●) *trans*-2-pentene.

summarizes these results. For reasons presented in the Discussion, we believe that the E value for *trans*-2-butene is about 0.6 kcal too low which would make the value of $\log A$ low by about 0.3 log units.

Discussion

The reaction of NO₂ with simple olefins is mechanistically and kinetically quite complex.⁴ Because of this, the easiest way to determine an upper limit for the rates of processes initiated by NO₂ addition to an olefin double bond is to determine the rate constant for the initial addition step. As is described below, this can be conveniently done by combining our present experimental results with the results of a number of thermochemical calculations.

Rate Constants. For the reaction



the rate constants, k_a and k_b , may be expressed in Arrhenius form as follows

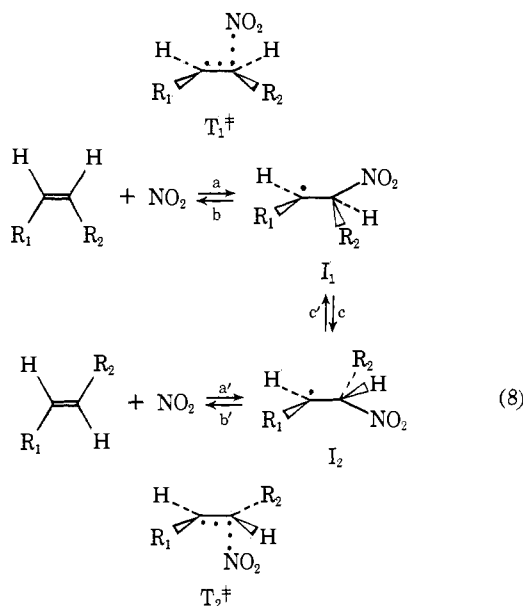
$$k_a = A_a e^{-E_a/RT} \text{ and } k_b = A_b e^{-E_b/RT} \quad (7)$$

(4) (a) J. H. Thomas, *Trans. Faraday Soc.*, **48**, 1142 (1952); (b) T. L. Cottrell and T. E. Graham, *J. Chem. Soc., London*, 556 (1953); (c) *ibid.*, 3644 (1954); (d) S. Jaffe in "Chemical Reactions in Urban Atmospheres," C. S. Tuesday, Ed., Elsevier, New York, N. Y., 1971; (e) S. C. Chao and S. Jaffe, *J. Chem. Phys.*, **56**, 1987 (1972); (f) B. V. Ashmead and J. H. Thomas, 14th Symposium on Combustion, The Combustion Institute, 1973, p 493.

where $k_a/k_b = K_{ab}$ and $-RT \ln K_{ab} = \Delta H_{ab}^{\circ,c} - T\Delta S_{ab}^{\circ,c}$. But $E_a = \Delta H_{ab}^{\circ,c} + E_b$, $A_a = A_b e^{\Delta S_{ab}^{\circ,c}/R}$, and $A_b = (ekT/h)e^{\Delta S_b^{\ddagger}/R}$. So, if $\Delta H_{ab}^{\circ,c}$, E_b , $\Delta S_{ab}^{\circ,c}$, and ΔS_b^{\ddagger} are known, k_a may be calculated. As is described in the Appendix, $\Delta H_{ab}^{\circ,c}$, $\Delta S_{ab}^{\circ,c}$, and ΔS_b^{\ddagger} can be calculated or estimated for a number of simple olefins by thermochemical or incremental methods.⁵ Therefore, if E_b can be determined, k_a can be calculated.

Two facts permit E_b to be determined. First, for simple olefins E_b is unlikely to be very sensitive to either the nature of the substituents (R_1 , R_2 , R_3 , and R_4) or the conformation (cis or trans) of the nitroalkyl radical **2**. Therefore, E_b ought to have nearly the same value for most simple olefins. Second, as is shown below, the rate constants (k_{cis} or k_{trans}) for the NO_2 catalyzed geometric isomerization of *cis*- or *trans*-2-butene or -2-pentene may be expressed as functions of only E_b and several fundamental constants (e , k , h) and calculable thermodynamic quantities (ΔS_b^{\ddagger} , $\Delta S_{ab}^{\circ,c}$, $\Delta H_{ab}^{\circ,c}$, and $\Delta H_I^{\circ,c}$, which is defined below). Therefore, our experimental rate constants may be used to calculate a value for E_b which will be applicable to most other simple olefins.

The NO_2 catalyzed geometric isomerization of 2-butene or 2-pentene most likely proceeds^{2a,3} by the following mechanism



Application of the steady state approximation to the nitroalkyl radical intermediates, I_1 and I_2 , yields the following expression, in which $K_{ij} = K_i/K_j$, for the rate of disappearance of *cis*-olefin.

$$-\frac{d[C]}{dt} = \left\{ \frac{K_{ab}k_c}{1 + K_{cb} + K_{c'b'}} \right\} [\text{NO}_2]_0 \times \left\{ [C]_0 - \left[1 + \frac{K_{a'b'}k_{c'}}{K_{ab}k_c} \right] [T] \right\} \quad (9)$$

(5) (a) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (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) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 221 (1969); (d) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 21 (1970).

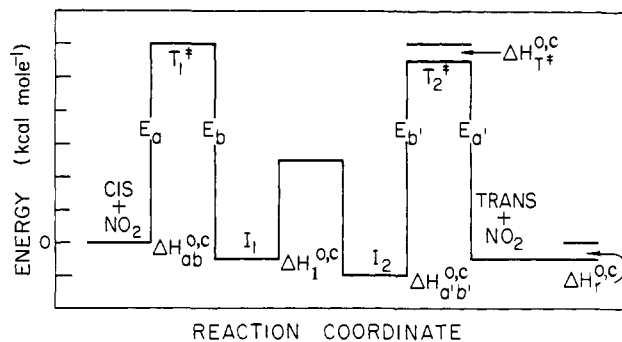


Figure 4. Schematic energy surface for the NO_2 catalyzed geometric isomerization of a simple olefin, illustrating the relations between the various thermochemical energy parameters used in this paper.

Because $K_{cb} \approx K_{c'b'} \gg 1$, for low conversions where $[T] \ll [C_0]$ this expression may be simplified and rearranged^{2a} to give

$$k_{cis} = k_a / \left(1 + \frac{K_{c'b'}}{K_{cb}} \right) \quad (10)$$

where

$$\frac{K_{c'b'}}{K_{cb}} = \frac{A_{c'}A_b}{A_cA_{b'}} e^{[(E_c - E_{c'}) + (E_b - E_{b'})]/RT}$$

Figure 4 schematically depicts the energy surface for the NO_2 catalyzed geometric isomerization of 2-butene or 2-pentene. In Figure 4 $\Delta H_r^{\circ,c}$ is the enthalpy change produced by the isomerization and

$$\Delta H_r^{\circ,c} = E_c - E_{c'} \quad (11)$$

$$= \Delta H_r^{\circ,c} + \Delta H_{a'b'}^{\circ,c} - \Delta H_{ab}^{\circ,c}$$

Because $\Delta H_r^{\circ,c}$ is known^{2b} and $\Delta H_{ab}^{\circ,c}$ and $\Delta H_{a'b'}^{\circ,c}$ are calculable (see Appendix), $\Delta H_r^{\circ,c}$ may be calculated.

Because the moments of inertia for rotation about the central carbon-carbon bond in the radicals, I_1 and I_2 , are the same,^{1a} $A_c = A_{c'}$. Because $\Delta S_b^{\ddagger} = \Delta S_{b'}^{\ddagger}$ (see supplemental material), $A_b = A_{b'}$. Therefore, since $E_b \cong E_{b'}$, eq 12 reduces to

$$k_{cis} = k_a / \{ 1 + e^{\Delta H_r^{\circ,c}/RT} \} \quad (12)$$

Appropriate substitution into eq 12 yields eq 13, where k_x represents either k_{cis} or k_{trans} and in which only E_b is unknown.

$$k_x = \frac{ekT}{h} \frac{e^{[(\Delta S_b^{\ddagger} + \Delta S_{ab}^{\circ,c})T - (E_b + \Delta H_{ab}^{\circ,c})]/RT}}{1 + e^{\Delta H_r^{\circ,c}/RT}} \quad (13)$$

Best agreement with experiment is obtained for $E_b = 11.8 \text{ kcal mol}^{-1}$. Table II compares the experimental

Table II. Comparison of Calculated and Experimental 298°K Rate Constants for the NO_2 Catalyzed Geometric Isomerization of the 2-Butenes and the 2-Pentenes

Olefin	$k_x^{298}, \text{ l. mol}^{-1} \text{ sec}^{-1}$	
	Calcd	Exptl
<i>cis</i> -2-Butene	0.150	0.159
<i>trans</i> -2-Butene	0.047	0.053
<i>cis</i> -2-Pentene	0.164 ^a	0.183
<i>trans</i> -2-Pentene	0.044 ^a	0.038

^a Because 2-pentene is unsymmetrical, it can isomerize by two reaction pathways distinguished by NO_2 addition at opposite ends of the double bond. Therefore, for 2-pentene the calculated values of k_x^{298} were obtained by summing the values of the rate constants calculated for each of the two isomerization pathways.

Table III. Arrhenius Parameters and Rate Constants Calculated for NO₂ Addition to the Double Bond of Ten Simple Olefins

Compd	Path ^a	Alkyl groups				$A_b \times 10^{-13}$, sec ⁻¹	k_b^{298} $\times 10^{-4}$, sec ⁻¹	$A_a \times 10^{-8}$, l. mol ⁻¹ sec ⁻¹	E_a , kcal mol ⁻¹	k_a^{298} , l. mol ⁻¹ sec ⁻¹
		R ₁	R ₂	R ₃	R ₄					
Acetylene		H	H			16.2	36.9	58.1	14.4	0.017
Ethylene		H	H	H	H	17.0	38.8	93.6	14.0	0.053
Propylene	I	CH ₃	H	H	H	2.52	5.75	7.40	13.6	0.009
	II	H	CH ₃	H	H	18.8	42.9	17.4	13.5	0.022
1-Butene	I	C ₂ H ₅	H	H	H	2.52	5.75	6.24	13.3	0.011
	II	H	C ₂ H ₅	H	H	18.8	42.9	12.0	11.7	0.348
Isobutene	I	CH ₃	H	H	CH ₃	12.0	27.3	37.5	12.4	0.301
	II	H	CH ₃	CH ₃	H	21.9	49.9	6.15	16.3	0.0001
<i>cis</i> -2-Butene		CH ₃	H	H	H	3.41	7.78	4.41	11.4	0.189
<i>trans</i> -2-Butene		H	CH ₃	H	H	3.41	7.78	7.44	11.6	0.023
1-Pentene	I	C ₃ H ₇	H	H	H	3.08	7.03	6.21	13.1	0.016
	II	H	C ₃ H ₇	H	H	18.8	42.9	10.8	11.6	0.321
<i>cis</i> -2-Pentene	I	C ₂ H ₅	CH ₃	H	H	3.41	7.78	2.05	11.2	0.140
	II	CH ₃	C ₂ H ₅	H	H	3.77	8.60	2.76	12.0	0.049
<i>trans</i> -2-Pentene	I	C ₂ H ₅	H	CH ₃	H	3.41	7.78	4.13	11.3	0.243
	II	H	C ₂ H ₅	H	CH ₃	3.77	8.60	5.59	12.1	0.085

^a For unsymmetrical olefins two reaction pathways are possible. Path I always denotes attack by NO₂ on that end of the double bond which is either less substituted or bears the smaller alkyl group. Thus, for propylene path I is initiated by NO₂ addition to the terminal methylene carbon and path II by NO₂ addition to the central methine carbon. ^b Because unsymmetrical olefins have two modes of addition (paths I and II), the overall rate constant for NO₂ addition to the double bond equals the sum of the rate constants for the pathways I and II.

rate constants (k_x) measured for these isomerizations to the values calculated using eq 13 with $E_b = 11.8$ kcal mol⁻¹, ΔH_1° equal to the values calculated using eq 11, and values of ΔS_b^{\ddagger} , ΔS_{ab}° , and ΔH_{ab}° taken from a supplemental table presented in the microfilm edition. As Table II shows, the agreement between calculation and experiment is remarkably good.

Table III presents the values of A_b , k_b , A_a , E_a , and k_a^{298} calculated for ten simple olefins using data taken from the supplemental tables and $E_b = 11.8$ kcal mol⁻¹. Only one direct comparison with experimental results other than our own is possible and that is for acetylene, for which a value of $k_a^{298} = 0.017$ l. mol⁻¹ sec⁻¹ may be calculated from the Arrhenius parameters [$\log A_a$, l. mol⁻¹ sec⁻¹ = 9.1; $E_a = 15.0$ kcal mol⁻¹] determined by Thomas^{4a} over the temperature range 170–220°. Again the agreement with experiment is remarkably good, which suggests that our calculated values of k_a^{298} are surely accurate to an order of magnitude and quite possibly to a factor of 2 or 3.

Arrhenius Parameters. Equation 12 provides a basis for comparing our calculated 2-butene and 2-pentene Arrhenius parameters for k_a to our experimental 2-butene and 2-pentene Arrhenius parameters for $k_x = k_{cis}$ or k_{trans} . To do this the denominator of eq 12 is approximated by an exponential

$$\alpha e^{\Delta h/RT} = 1 + e^{\Delta H_1^{\circ}/RT} \quad (14)$$

Substitution of this approximation into eq 12 and expression of k_a and k_x in Arrhenius form yields

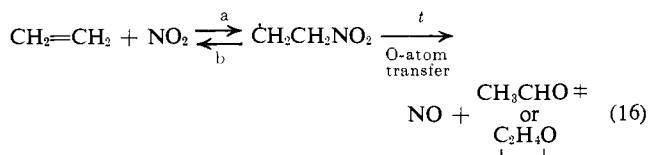
$$k_x = A_x e^{-E_x/RT} = \frac{A_a}{\alpha} e^{-(E_a + \Delta h)/RT} \quad (15)$$

Division of the first derivative of eq 15 by that equation yields an expression for Δh as a function only of ΔH_1° for which values are available. Since α can be determined from Δh , A_a/α and $E_a + \Delta h$ can be calculated. Table IV summarizes the results of these calculations. Since the comparison is pertinent, Table IV also compares our calculated Arrhenius parameters for k_a for acetylene to the experimental values of Thomas.^{4a}

Table IV shows that except for *trans*-2-butene the calculated Arrhenius preexponential factors are all low⁶ by a factor of about 2 and the calculated activation energies are all low by about 0.4 kcal mol⁻¹. This suggests that our experimental Arrhenius parameters for *trans*-2-butene are most probably in error and ought to be changed to values of $E_x = 12.8$ kcal mol⁻¹ (in order to make $E_x^{cis} - E_x^{trans} = \Delta H_1^{\circ} = 1.0$ kcal mol⁻¹ and $A_x = 9.6 \times 10^7$ l. mol⁻¹ sec⁻¹ (in order to make $A_x e^{-E_x/RT} = k_x = 0.053$ l. mol⁻¹ sec⁻¹, when $T = 298^\circ\text{K}$ and $E_x = 12.8$ kcal mol⁻¹).

Jaffe has measured the temperature dependence (25 to 100°) of the rate of disappearance of NO₂ upon reaction with seven simple olefins.^{4d} Regardless of the olefin used, the reaction was second order overall and first order both in olefin and NO₂. Table V tabulates the Arrhenius parameters determined by Jaffe for these reactions.

Comparison of the Arrhenius parameters in Table V to those in Table IV strongly indicates that the rate-determining step of Jaffe's reactions was not addition of NO₂ to the olefin double bond. For ethylene Jaffe has proposed^{4d} the following initial reaction sequence



If $k_t < k_a \ll k_b$, which our calculations show to be the case, then $k_{obsd} = (k_a/k_b)k_t$ and therefore

$$E_t = E_{obsd} - \Delta H_{ab}^{\circ} \quad (17)$$

$$\log A_t = \log A_{obsd} - \frac{\Delta S_{ab}^{\circ}}{2.3R}$$

Substitution into eq 17 of values of ΔH_{ab}° and ΔS_{ab}° taken from the supplemental tables and of Jaffe's values

(6) In our calculation of ΔS_b^{\ddagger} (see Appendix) we have assumed a two-thirds decrease in the barrier to internal rotation of the NO₂ group. If passage to the transition state (T^\ddagger) actually lowers this barrier to zero, then our calculated preexponential factors (A_a) would all increase by a factor of about 1.4.

Table IV. Calculated and Experimental Arrhenius Parameters for the 2-Butenes, the 2-Pentenes, and Acetylene

Compd	Path	ΔH_1° , kcal mol ⁻¹	Δh , kcal mol ⁻¹	α	Calcd		Exptl	
					$A_x = A_a/\alpha$, l. mol ⁻¹ sec ⁻¹	$E_x = E_a + \Delta h$, kcal mol ⁻¹	A_x , l. mol ⁻¹ sec ⁻¹	E_x , kcal mol ⁻¹
<i>cis</i> -2-Butene		-0.8	-0.17	1.30	3.4×10^7	11.3	7.2×10^7	11.8
<i>trans</i> -2-Butene		0.8	0.63	1.68	4.4×10^7	12.3	4.5×10^7	12.1
<i>cis</i> -2-Pentene	I	-1.1	-0.15	1.49	1.4×10^7	11.0	3.1×10^7	11.2
	II	-1.1	-0.15	1.49	1.9×10^7	11.8		
<i>trans</i> -2-Pentene	I	1.1	0.95	1.49	2.8×10^7	12.2	5.2×10^7	12.5
	II	1.1	0.95	1.49	3.8×10^7	13.0		
C ₂ H ₂			0	1	5.8×10^8	14.4	1.3×10^9	15.0

Table V. Arrhenius Parameters for O-Atom Transfer by β -Nitroalkyl Radicals

Compd	E_{obsd}^a	Log A_{obsd}^a	E_t	Log A_t
Ethylene	8.1	3.3	5.9	8.5
Propylene	7.9	3.5	6.2	9.5
1-Butene	7.3	3.4	7.4	9.6
Isobutene	4.0	1.6	3.4	7.1
<i>cis</i> -2-Butene	5.4	2.4	5.8	8.1
<i>trans</i> -2-Butene	6.4	3.2	6.6	9.1
1-Pentene	7.2	3.2	7.4	9.4

^a Reference 5d.

of E_{obsd} and log A_{obsd} yields the values of E_t and log A_t listed in Table V. With the exception of isobutene, the values of E_t or log A_t are quite similar as would be expected for substrates bearing different alkyl substituents but reacting *via* the same transition state. However, the values of log A_t appear⁷ to be low by at least two orders of magnitude, which suggests that these reactions do not have a cyclic four-center O-atom transfer as their rate-determining step.

Air Pollution. Equation 18 formulates the ratio of the rate of consumption of an olefin (OI) by ozone (R_{O_3}) to that by nitrogen dioxide (R_{NO_2}).

$$\frac{R_{O_3}}{R_{NO_2}} = \frac{k_{O_3} [O_3] [OI]}{k_{NO_2} [NO_2] [OI]} \quad (18)$$

Substitution into this equation of a maximum value for k_{NO_2} and minimum values for k_{O_3} and the ratio of concentrations, $[O_3]/[NO_2]$, will yield a minimum value for the rate ratio, R_{O_3}/R_{NO_2} .

In polluted urban atmospheres⁸ the concentration of NO_2 rarely exceeds that of O_3 by more than a factor of 100. The rate constant for addition of NO_2 to an olefin double bond (k_a) must be greater than the rate constant for consumption of NO_2 by reaction with that olefin (k_{NO_2}). Table III shows that for simple olefins $k_a^{\text{max}} \approx 10^{-1}$. Rate constants for the consumption of O_3 by reaction with simple olefins⁹ range from 10^3 to 10^5 l. mol⁻¹ sec⁻¹, so $k_{O_3}^{\text{min}} \approx 10^3$. Substitution of these values in eq 20 yields a minimum value of $R_{O_3}/R_{NO_2} = 10^2$, which shows that atmospheric reaction pathways initiated by NO_2 addition to an olefin double bond cannot possibly be significant in the bulk consumption of olefin pollutants.

(7) (a) S. W. Benson, private communication; (b) ref 4d; (c) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967).

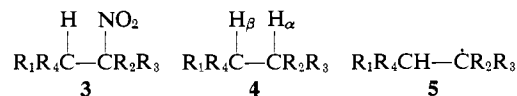
(8) B. D. Tebbens, "Air Pollution," Vol. 1, 2nd ed, A. C. Stern, Ed., Academic Press, New York, N. Y., 1968, p 23.

(9) H. S. Johnston, J. N. Pitts, Jr., J. Lewis, L. Zafonte, and T. Motterhead, "Atmospheric Chemistry and Physics" in "Project Clean Air," Vol. 4, E. S. Starkman, Ed., University of California, 1970, Task Force Assessments.

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Appendix: Calculation of Thermochemical Quantities for Reaction 6

Calculation of $\Delta H_{\text{ab}}^\circ$. $\Delta H_{\text{ab}}^\circ$ may be calculated in at least two ways from the data presented in the microfilm edition.



$$\Delta H_{\text{ab}}^\circ = D_\pi(1) - D_{\text{C-NO}_2}(2) \quad (\text{A1})$$

$$\Delta H_{\text{ab}}^\circ = \Delta H_f^\circ(2) - \Delta H_f^\circ(1) - \Delta H_f^\circ(\text{NO}_2) \quad (\text{A2})$$

$D_\pi(1)$, $D_{\text{C-NO}_2}(2)$, and $\Delta H_f^\circ(2)$ are not directly available and must be calculated.

$$D_\pi(1) = D_{\text{C-H}_\alpha}(4) + D_{\text{C-H}_\beta}(4) - D_{\text{H-H}}(\text{H}_2) - \Delta H_{\text{hydrogenation}}(1) \quad (\text{A3})$$

Taking $D_{\text{C-NO}_2}(3)$ to be a reasonable model for $D_{\text{C-NO}_2}(2)$ gives

$$D_{\text{C-NO}_2}(2) = \Delta H_f^\circ(5) + \Delta H_f^\circ(\text{NO}_2) - \Delta H_f^\circ(3) \quad (\text{A4})$$

Taking $D_{\text{C-H}_\beta}(4)$ to be a reasonable model for $D_{\text{C-H}}(3)$ gives

$$\Delta H_f^\circ(2) = \Delta H_f^\circ(3) - \Delta H_f^\circ(\text{H}) + D_{\text{C-H}_\beta}(4) \quad (\text{A5})$$

Appropriate combination of these equations followed by substitution of the values listed in the microfilm edition now permits two values to be calculated for $\Delta H_{\text{ab}}^\circ$. Conversion of the average of these two values for $\Delta H_{\text{ab}}^\circ$ to concentration units gives $\Delta H_{\text{ab}}^{\circ,c}$. The results of these calculations are presented in the microfilm edition.

Calculation of $\Delta S_{\text{ab}}^\circ$

$$\Delta S_{\text{ab}}^\circ = S^\circ(2) - S^\circ(1) - S^\circ(\text{NO}_2) \quad (\text{A6})$$

Data sufficient for the calculation of $S^\circ(2)$ are unavailable. Instead, $S^\circ(2)$ has been estimated from $S^\circ(3)$ using the methods of Benson and coworkers.⁵ Appropriate corrections^{5c} were made for changes in mass, spin, symmetry, and moments of inertia and rotational

barriers¹⁰ of internal rotors. Where values of $S^\circ(3)$ were lacking, they were estimated by incremental or group additivity methods.⁶ Conversion of ΔS_{ab}° to concentration units gives $\Delta S_{ab}^{\circ,c}$. The results of these calculations are tabulated in the microfilm edition.

Estimation of ΔS_b^\ddagger . ΔS_b^\ddagger was estimated by summing the changes in rotational¹⁰ and vibrational¹⁴ entropy

(10) Both molecular dimensions¹¹ and A values¹² suggest that, when estimating rotational barriers, a methyl group ought to be a satisfactory model for a nitro group. Accordingly, the saturated alkane, obtained by replacing the nitro group in the nitroalkane **3** by a methyl group, was used as a model for estimating rotational barriers in the nitroalkane **3**. For example, propane was used as a model for nitroethane. Then, using the methods of Benson and coworkers,⁵ rotational barriers in the nitroalkyl radical **2** or the transition state T^\ddagger were estimated from the rotational barriers estimated for the nitroalkane **3**. Rotational barriers in the saturated alkane model compounds were based on literature data.¹³

(11) G. H. Wagniere, "The Chemistry of the Nitro and Nitroso Group," H. Feuer, Ed., Interscience, New York, N. Y., 1969, Part 1, p 1.

(12) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

(13) (a) J. Dale, *Tetrahedron*, **22**, 3373 (1966); (b) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968); (c) ref 5d.

(14) (a) Torsional frequencies (ω) of the three electron bonds in the transition state (T^\ddagger) were taken to be one-half the magnitude of those estimated for the structurally identical nitro olefin having a full double bond. Torsional frequencies for the nitro olefin were calculated using the formula $\omega \propto [(M_1 + M_2)/M_1M_2]^{1/2}$. In all calculations the torsional frequency of the olefin, obtained by replacing the NO_2 group in the nitro olefin by a CH_3 group, was used as the reference frequency.^{5d} Other vibrational frequencies were taken from the following references: (b) N. B. Coltrup, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964; (c) T. Shimanouchi, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. **6** (1967); (d) N. L. Alpert, W. E. Keiser, and H. A. Szymanski, "IR; Theory and Practice of Infrared Spectroscopy," Plenum Press, New York, N. Y., 1970; (e) ref 5d.

produced in the nitroalkyl radical, I, upon passage to the transition state, T^\ddagger . Equation A7 expresses this summation.

$$\begin{aligned} \Delta S_b^\ddagger = & S^\circ[(C-\text{NO}_2)_{rc} + (C-C)_s^{1300} + \\ & (C-C \cdot \text{NO}_2)_b^{185} + 2(\text{NO}_2)_{1e \text{ rook}}^{170} + (C(\cdot) \cdot \text{NO}_2) + \\ & (C-C)_t] - S^\circ[(C-\text{NO}_2)_s^{825} + (C-C)_s^{1000} + \\ & (C-C-\text{NO}_2)_b^{370} + 2(\text{NO}_2)_{2e \text{ rook}}^{500} + (C(\cdot) \cdot \text{NO}_2) + \\ & (C(\cdot) \cdot C)] + R \ln \{ \sigma_{(2)} / \sigma_{(T^\ddagger)} \} \quad (\text{A7}) \end{aligned}$$

Equation A7 was formulated using the methods and terminology of Benson and O'Neal.^{5d} In formulating eq A7 all entropy terms of magnitude less than 0.1 gibbs mol^{-1} were neglected. The values of ΔS_b^\ddagger computed using eq A7 are listed in the microfilm edition.

Supplementary Materials Available. Two tables will appear following these pages in the microfilm edition of this volume of the journal. The first tabulates our experimental rate constants and the conditions of their measurement. The second summarizes the thermochemical quantities used in or calculated by the thermochemical methods described in the Appendix. Photocopies of the supplementary material from this paper only or microfiche (105 \times 148 nm, 24 \times reduction, negatives) containing all of the supplementary material for papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6549.

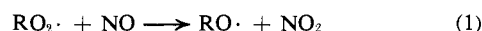
A Long Path Infrared Spectroscopic Study of the Reaction of Methylperoxy Free Radicals with Nitric Oxide

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Abstract: The reaction of NO with CH_3O_2 radicals generated in the photooxidation of $\text{CH}_3\text{N}_2\text{CH}_3$ at $\lambda > 320$ nm was investigated at $23 \pm 2^\circ$ using long path infrared and gas chromatographic techniques. Reaction conditions were: $\text{CH}_3\text{N}_2\text{CH}_3$, 33–369 mTorr; O_2 , 2200–5320 mTorr; and NO, 25–76 mTorr, at a total pressure of 760 Torr (He or N_2). At short photolysis times, CH_3ONO and NO_2 were both identified as products with quantum yields of 1.7 ± 0.2 and 1.9 ± 0.3 , respectively. HCHO was qualitatively identified in several runs by the chromotropic acid test. At longer reaction times, methyl nitrate also accumulated. These results suggest that the reaction $\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} \cdot + \text{NO}_2$ (7) is the only path for the reaction of methylperoxy radicals with nitric oxide under these conditions. $\text{CH}_3\text{O} \cdot$ is then removed by the reactions: $\text{CH}_3\text{O} \cdot + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2$ (9a), $\text{CH}_3\text{O} \cdot + \text{NO}_2 \rightarrow \text{HCHO} + \text{HONO}$ (9b), $\text{CH}_3\text{O} \cdot + \text{NO} \rightarrow \text{CH}_3\text{ONO}$ (8a), and $\text{CH}_3\text{O} \cdot + \text{NO} \rightarrow \text{HCHO} + \text{HNO}$ (8b).

The reaction of alkylperoxy radicals with nitric oxide is generally assumed^{1–3} to proceed by the oxidation of nitric oxide to nitrogen dioxide with formation of an alkoxy radical



(1) H. Niki, E. E. Daby, and B. Weinstock, *Advan. Chem. Ser.*, No. **113**, 16 (1971).

(2) A. P. Altshuller and J. J. Bufalini, *Photochem. Photobiol.*, **4**, 97 (1965).

(3) T. A. Hecht and J. A. Seinfeld, *Environ. Sci. Technol.*, **6**, 47 (1972).

Reaction 1 is believed to be an important route for oxidizing NO to NO_2 in photochemical smog. In addition, the alkoxy radical, $\text{RO} \cdot$, may react further in the atmosphere to produce $\text{HO}_2 \cdot$ ⁴ which also converts NO to NO_2 . However, a mass spectrometric study⁵ in-

(4) J. Heicklen, K. Westberg, and N. Cohen, Center for Air Environmental Studies Report No. 115-69, The Pennsylvania State University, 1969.

(5) C. W. Spicer, A. Villa, H. A. Wiebe, and J. Heicklen, *J. Amer. Chem. Soc.*, **95**, 13 (1973).