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Relative Rates of Reactions of Oxygen Atoms with Olefins*

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Relative rates of addition of oxygen atoms in their ground electronic state to a number of olefins in the gas phase have been determined at room temperature. These reactions exhibit the following regularities: (1) systematic variation of the rates with the structure of the olefins; (2) specificity with respect to the position of addition of oxygen atoms; and (3) partial molecular rearrangement of the addition products according to definite rules. The observed structural effects and some close analogies with certain olefin addition reactions in solution are discussed in the light of electronic theories of organic chemical reactions. A comparison is made of the absolute values of the rate constants of the reactions of oxygen atoms with olefins, derived from various sources.

INTRODUCTION

THE present work is a part of a study of the reactions of oxygen atoms with different organic compounds. The two objectives of these investigations are (1) to establish the general mechanism and the type of products formed, and (2) to obtain information on the reaction rates. For the reactions of oxygen atoms with mono-olefins, following a brief preliminary communication,[1] the first of the two aspects of the investigation has been reported in detail.[2] The present paper deals with the relative rates of reactions of oxygen atoms with a number of mono-olefins and includes also a discussion of the structural effects observed in these processes.

Oxygen atoms are produced by mercury photosensitized decomposition of nitrous oxide.[3] Inasmuch as the spin conservation rule is obeyed in this process, the oxygen atoms are formed in their ground, triplet $O(^3P)$, state. A strong support for this view is provided by a comparison of some of these reactions with the corresponding reactions with oxygen atoms obtained by photolyzing NO_2.[4]

EXPERIMENTAL

The conventional apparatus used in this work and the analytical methods employed have been described previously.[2] The reactants were the best available grades and were thoroughly degassed and bulb to bulb distilled *in vacuo* before use.

RESULTS

The determination of relative rate constants in the present work is based on the reaction scheme

$$\mathrm{Hg}+h\nu\rightarrow Hg^*,$$

$$\mathrm{Hg}^*+\mathrm{N_2O}\rightarrow\mathrm{Hg}+\mathrm{N_2}+\mathrm{O},$$

$$\mathrm{O}+A_1\rightarrow\alpha_1P_1+\cdots, \tag{1}$$

$$\mathrm{O}+A_2\rightarrow\alpha_2P_2+\cdots, \tag{2}$$

where A_1 and A_2 are two olefins competing for oxygen atoms, P_1 is one of the products of reaction (1), $\alpha_1=\Delta P_1/\Delta N_2$ when only A_1 and no A_2 is present (i.e., it is the amount of P_1 produced per oxygen atom reacting with A_1). Hence, α_2 and P_2 have analogous significance for reaction (2).

In order to be useful for determination of relative rate constants, the rates of formation of the products P_1 and P_2 per oxygen atom reacting with A_1 and A_2, respectively, must be independent of whether only one or both A_1 and A_2 are present. This consideration is satisfied at sufficiently high total pressures by most of the products of these reactions since they are mostly formed by direct addition of the oxygen atoms to the olefinic double bond and subsequent molecular rearrangement, and not by combination of free radicals.[1,2] Sufficiently high total pressures are necessary to ensure collisional deactivation since the products possess excess energy when formed.[2] If the initial concentrations $(A_1)i$ and $(A_2)i$ are sufficiently high so that they remain essentially unaltered in the course of the reaction, then the ratio of the rate constants is given by

$$(k_1/k_2)=(\alpha_2/\alpha_1)(\Delta P_1/\Delta P_2)[(A_2)i/(A_1)i]. \tag{1}$$

If oxygen atoms are consumed only in reactions (1) and (2), then

$$(1/\alpha_1)\Delta P_1+(1/\alpha_2)\Delta P_2=\Delta \mathrm{N}_2, \tag{2}$$

which, when combined with (1), gives

$$\Delta\mathrm{N}_2/\Delta P_1=(1/\alpha_1)\{1+(k_2/k_1)[(A_2)i/(A_1)i]\} \tag{3a}$$

or

$$k_1/k_2=[(A_2)i/(A_1)i][(\alpha_1\Delta\mathrm{N}_2/\Delta P_1)-1]^{-1}. \tag{3b}$$

When the concentrations of the olefins change substantially in the course of the reaction, then, assuming a steady-state concentration of oxygen atoms and no other reactions involving oxygen atoms and the two olefins, the ratio of the rate constants is given by the expression

$$k_1/k_2=\log[(A_1)f/(A_1)i/\log[(A_2)f/(A_2)i], \tag{4a}$$

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* Contribution No. 4971 from the National Research Council, Ottawa, Canada.

[1] R. J. Cvetanović, J. Chem. Phys. **25**, 376 (1956).

[2] R. J. Cvetanović, Can. J. Chem. **36**, 623 (1958).

[3] R. J. Cvetanović, J. Chem. Phys. **23**, 1203 (1955).

[4] S. Sato and R. J. Cvetanović, Can. J. Chem. **36**, 970 (1958).

TABLE I. The mean values obtained for the relative rate constants of the reactions of oxygen atoms with olefins in the gas phase at 25°C.

A_1	A_2	Mean k_1/k_2	Method of determination (equation used)
C_4H_8-1	*cis*-C_4H_8-2	0.28	GLC(4c)
C_4H_8-1	*iso*-C_4H_8	0.237	GLC(4c)
C_4H_8-1	*cis*-$C_5H_{10}-2$	0.263	GLC(4c)
C_4H_8-1	C_2H_4	6.3	GLC(3b)
C_4H_8-1	C_3H_6	1.06	GLC(1, 3b)
iso-C_4H_8	*trans*-C_4H_8-2	0.885	GLC(4c)
cis-C_4H_8-2	C_2H_4	22	CO[a] (6)
cyclopentene	*iso*-C_4H_8	1.26	C_2H_4[b] (5)
cyclopentene	C_4H_8-1	5.16	C_2H_4[b] (5)
cyclopentene	$C_2(CH_3)_4$	0.290	C_2H_4[b] (5)
cyclopentene	$C_2(CH_3)_4$	0.284	GLC (4c)

[a] Based on CO production for various ratios of concentrations of *cis*-C_4H_8-2 and C_2H_4 (Fig. 1).

[b] C_2H_4 produced in the reaction of oxygen atoms with cyclopentene was determined by recovering and measuring manometrically the C_2 fraction and analyzing for C_2H_4 and any C_2H_6 present by mass spectrometer.

or

$$k_1/k_2 = \log\{1-[\Delta A_1/(A_1)i]\}/\log\{1-[\Delta A_2/(A_2)i]\}, \tag{4b}$$

or

$$k_1/k_2 = \log\{1-[\Delta P_1/\alpha_1(A_1)i]\}/\log\{1-[\Delta P_2/\alpha_2(A_2)i]\}. \tag{4c}$$

$(A_1)f$ and $(A_2)f$ are the final concentrations of A_1 and A_2, respectively. For small conversions these expressions reduce to (1). Here again, (4c) can be combined with (2) and then k_1/k_2 can be determined from $\Delta P_2/\alpha_2$, ΔN_2, $(A_1)i$ and $(A_2)i$ without measuring $\Delta P_1/\alpha_1$, i.e.,

$$k_1/k_2 = \log\{1-[\Delta N_2/(A_1)i] + [\Delta P_2/\alpha_2(A_1)i]\}/\log\{1-[\Delta P_2/\alpha_2(A_2)i]\}. \tag{5}$$

Any of the expressions (1), (3), (4), or (5) can be used, under appropriate conditions, to determine k_1/k_2. For most determinations in the present work Eq. (4c) was used. The products formed on addition of oxygen atoms to the olefins, isomeric epoxides, and carbonyl compounds, were recovered and their relative amounts for different ratios of the initial concentrations of the two olefins were determined from gas liquid chromatography (GLC)[2] peak areas. The results are summarized in Table I, where the mean values obtained for the relative rate constants are given and the analytical method and the equation used are indicated. In most cases it was possible to choose sufficiently high concentrations of the two olefins so that they were changed relatively little in the course of the reaction and the application of Eq. (4c) instead of (1) amounted only to a small correction. Using several hundred millimeters of N_2O and only a few millimeters of the olefins prevented any appreciable decomposition of the olefins as a result of direct quenching especially at the higher total pressures employed where they readily undergo collisional deactivation.[5]

The ratio of the rate constants for C_4H_8-1 and C_2H_4 was determined from the GLC peak areas of the α-butene oxide (formed from C_4H_8-1) using Eq. (3b). The ratio for *cis*-C_4H_8-2 and C_2H_4 was obtained from the rates of CO formation at different concentration ratios of the two olefins and using the expression

$$\frac{(R_{CO}^*-R_{CO})_2}{(R_{CO}-R_{CO}^*)_1} = \frac{k_1}{k_2}\frac{(A_1)}{(A_2)}, \tag{6}$$

where $R_{CO}=\Delta CO/\Delta N_2$ and R_{CO}^* is the analogous quantity when only one olefin is present. This expression is based on the assumption that the rate of CO formation per oxygen atom reacting with either of the two olefins is independent of whether the other olefin is present or not. This is probably not strictly correct. However, a fairly good linear plot through the origin is obtained (Fig. 1) and the slope gives the k_1/k_2 value shown in Table I. The possibility of using Eq. (6) in this case is based on the fact that CO is an important product in the reaction of O with C_2H_4($R_{CO}^*=0.44$ for the employed conditions) and a minor one in the case of *cis*$-C_4H_8-2$($R_{CO}^*=0.036$). In an analogous manner the production of CH_4 differs appreciably in the two cases, but it is much smaller than that of CO and a plot similar to Fig. 1, although leading to a

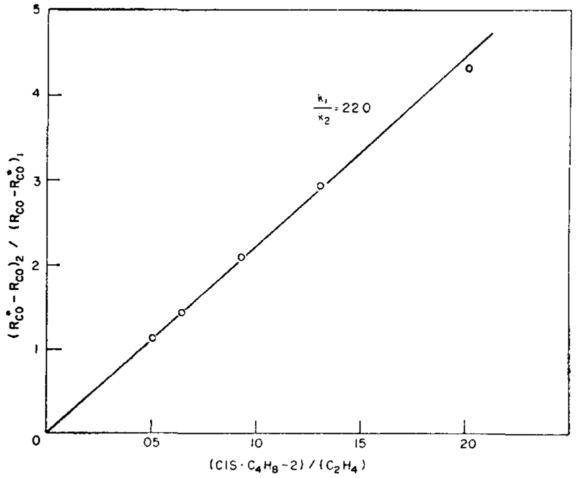

FIG. 1. Plot of the quantities in Eq. (6) for *cis*-C_4H_8-2 and C_2H_4. [25±1°C; 300 mm N_2O; total (*cis*-C_4H_8-2+C_2H_4) 22 mm; irradiation time 120 min; approximately 14 μmoles of N_2 produced in each experiment; $(R_{co}^*)_1=0.036$, $(R_{co}^*)_2=0.440$; subscripts 1 and 2 refer to *cis*-C_4H_8-2 and C_2H_4, respectively].

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[5] E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1954), second edition, pp. 411–456.

TABLE II. Relative rate constants for different series of addition reactions to olefins (based on the present work and literature values, as indicated).

	Reaction series							
Olefin	O[a]	Peracetic acid[b]	O_3[c]	Br_2[d]	CBr_2[e]:	CCl_3[f]	CH_3[g]	H[h]
Ethylene	0.038	0.002	0.0040	0.18			0.94	0.88
Propylene	0.23	0.046	0.0092	0.36			0.61	0.28
1-Butene	0.24					0.19	0.75	
1-Pentene		0.047	0.0078				0.68	
1-Hexene		0.052	0.015		0.07		0.71	
1-Octene		0.054	0.012			0.19		
1-Decene		0.051	0.016				0.61	
Isobutene	1.00	1.00		1.00	1.00	1.00	1.00	1.00
2-butene (*trans*)	1.13						0.19	1.09
2-Butene (*cis*)	0.84	1.01[i]					0.094	1.40
2-Pentene (*cis*)	0.90	1.03[i]						1.01
2-Hexene		1.08						
3-Hexene		1.40						
Cyclopentene	1.20	2.12			0.5	0.15		
Cyclohexene		1.40			0.4	0.045		1.39
2-Methyl-2-butene		13.5		1.9	3.2	0.17		1.28
2,3 Dimethyl-2-butene	4.18	Very fast		2.5	3.5			0.84

[a] Present work.
[b] See references 10, 11, and 15.
[c] R. D. Cadle and C. Schadt, J. Am. Chem. Soc. **74**, 6002 (1952).
[d] S. V. Anantakrishnan and C. K. Ingold, reference 12.
[e] See reference 6.
[f] Taken from reference 6.
[g] Buckley, Leavitt, and Szwarc, J. Am. Chem. Soc. **78**, 5557 (1956).
[h] Allen, Melville, and Robb, Proc. Roy. Soc. (London) **A218**, 311 (1953).
[i] Mixture of *cis* and *trans*.

roughly similar value of k_2/k_1, shows a large scatter of points.

In the later stages of the present work it has been found that ethylene is a product of the reaction of O atoms with cyclopentene while it is not formed in the other reactions studied. With cyclopentene alone it was found that $\Delta C_2H_4/\Delta N_2 = 0.265$ and when another substance reacting with O atoms (without thereby producing ethylene) is present this value decreases. Equation (5) can therefore be used to determine k_2/k_1 taking $\Delta P_2 = \Delta C_2H_4$ and $\alpha_2 = 0.265$. This technique is potentially very useful since ethylene can be readily recovered and measured accurately. Some determinations have been made using this technique and the mean results are given in Table I. With tetramethyl ethylene this method has been directly compared in the same experiments with the GLC technique [Eq. 4(c)] and the two methods gave remarkably close values in each of the four determinations made (the mean values are shown in Table I).

It is evident from Table I that there is good mutual consistency of the k_1/k_2 values in the cases where cross determinations have been made. Nevertheless, it is estimated that the uncertainty in most of these values is probably of the order of about 10 to 15%. It is hoped that with additional precautions and with the use of the cyclopentene technique the figures can be improved. For the purpose of the following discussion, however, the present accuracy is quite satisfactory.

DISCUSSION

The relative rate constants of oxygen atoms obtained in this work, taking arbitrarily the rate constant of the reaction with isobutene as unity, are given in column 1 of Table II. Literature data for a number of addition reactions to the same and some other olefins are given for comparison in columns 2–8. The rate constants of the reactions with isobutene are again taken as unity, except in the case of the ozone reactions where the reaction with isobutene has not been studied and the figures represent the absolute values as given in the original work (the units are μatmos^{-1} min^{-1}).

The relative rate constants of the reactions of oxygen atoms with olefins (k_0) given in Table II show a strong dependence on the number of alkyl groups attached directly to the doubly bonded carbon atoms. The trend is shown in Fig. 2 where $\log k_0$ is plotted against the number of alkyl groups attached to the doubly bonded carbon atoms. The rate constant is primarily dependent on the number of the substituent alkyl groups and the nature of these groups seems to have at best only a small effect. A very close analogy in this respect is found in the reactions of peracetic acid, bromine, and CBr_2 with olefins (Table II, columns 2, 4, and 5 respectively). The very limited information on ozone reactions (Table II, column 3) seems to suggest a similar trend, although more extensive experimental information on these reactions is necessary.

The close similarity in the trends in the rate con-

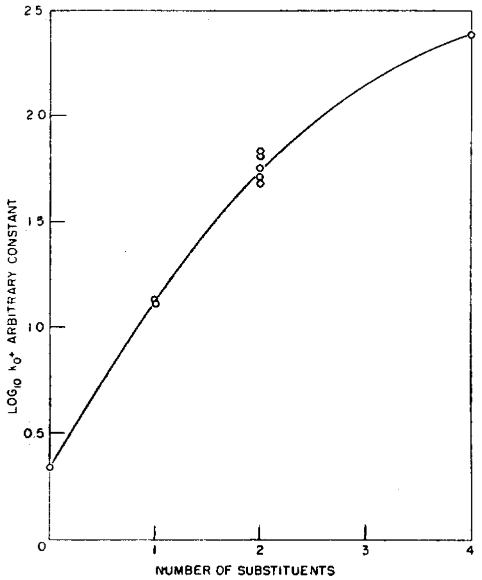

FIG. 2. Variation of $\log k_0$ with the number of alkyl groups substituted in the molecule of ethylene. (k_0 are the relative rate constants of oxygen atom reactions.)

stants of these five types of reactions (including here tentatively ozone reactions as well) is evident from the linear plots in Fig. 3 of the values of $\log k$ against $\log k_0$, where k_0 are the relative rate constants of oxygen atom reactions for the same olefins. Skell and Garner have pointed out previously[6] this type of correlation for the reactions of olefins with peracetic acid, Br_2, and CBr_2, and the lack of such a correlation with the corresponding CCl_3 reactions (column 6, Table II).

Numerous examples of linear correlations of the logarithms of rate constants for different series of reactions in solution are well known.[7] Another not infrequently observed relationship is the linear dependence of the logarithms of the rate constants of a series of reactions between one fixed and a number of variable reactants on a physical property of the latter. This type of correlation appears also to be exhibited by the reaction series of Fig. 3. Thus, for example, for the reactions of oxygen atoms, there is a linear dependence of $\log k_0$ on the ionization potentials (I), heats of hydrogenation (ΔHh), and the spectroscopic excitation energies (E ex) of the olefins, as shown in Fig. 4.

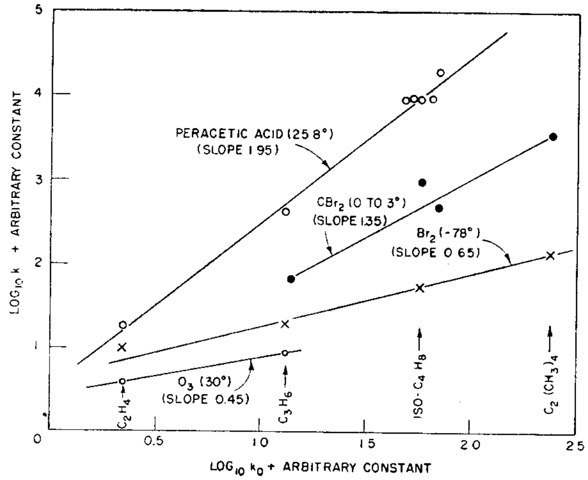

FIG. 3. $\log k$–$\log k_0$ plots. (The rate constants and literature sources are shown in Table II. For CBr_2 additions the values of k for propylene and butene-1 are not available and k for pentene-1 is plotted against k_0 for butene-1. k_0 are the relative rate constants of oxygen atom reactions.)

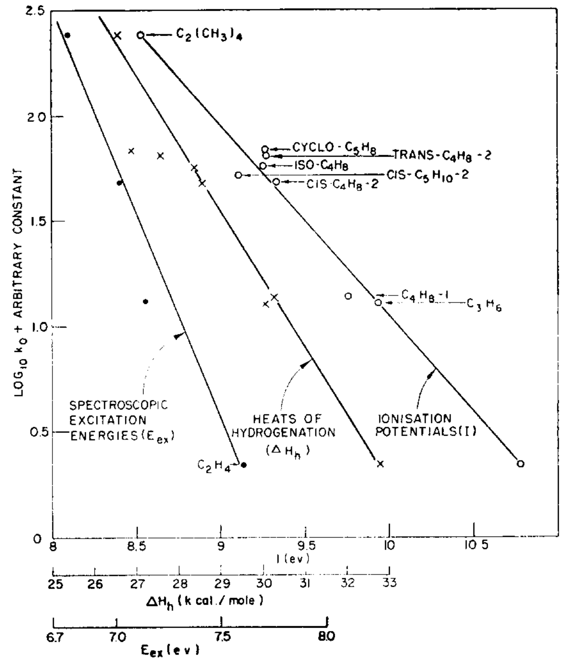

FIG. 4. Plot of $\log k_0$ against the ionization potentials, heats of hydrogenation and the spectral excitation energies. [The values of the ionization potentials have been obtained from Dr. F. P. Lossing. The heats of hydrogenation are from J. B. Conant and J. B. Kistiakowsky, Chem. Revs. **2a**, 181 (1937). The values of the spectral excitation energies are for the N–V transition and have been taken from R. S. Mulliken, Revs. Modern Phys. **14**, 265 (1942). k_0 are the relative rate constants of oxygen atom reactions.]

The two types of correlation are of considerable interest for the study of the effects of molecular structure on chemical reactivity and it seems worthwhile to summarize briefly some of their implications. There is, as a rule, a certain amount of scatter of points in such plots, only partly due to experimental errors, indicating a superposition of minor structural effects upon a major trend. For the study of the latter it may be first assumed that the linear plots are perfect.

A linear $\log k - \log k$ plot implies the validity of the expression

$$\log k_i' = S \log k_i'' + C, \tag{7}$$

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[6] P. S. Skell and A. Y. Garner, J. Am. Chem. Soc. **78**, 5430 (1956).

[7] L. P. Hammett, *Physical Organic Chemistry* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. VII.

where S is the slope, C the intercept and the superscripts $'$ and $''$ refer to two series of reactions involving the same homologous reactants. The linearity is assured if S has a constant value, i.e.,

$$S=(\log k_i'-\log k_j')/(\log k_i''-\log k_j'') \qquad (8)$$

for any two members (i, j) of the homologous series of reactants. A necessary consequence of condition (8) is that

$$\log k_i'-\log k_j'=\rho'(\sigma_i-\sigma_j) \qquad (9)$$

and

$$\log k_i'=\rho'\sigma_i+\alpha', \qquad (10)$$

where ρ' and α' are constants for the reaction series while σ_i, σ_j are constants characteristic of the particular reactants (i, j) and equal in the two reaction series (and in any other reaction series giving linear $\log k$–$\log k$ plots with the two). Equation (9) is the well-known empirical relationship used by Hammett to compare the effects of substituents in some reactions of aromatic compounds. [The first, unsubstituted member of the series was then arbitrarily taken as the standard, i.e., the reactant (j) in the equation.] A considerable number of values of the Hammett ρ and σ functions relative to arbitrarily chosen standards have been accumulated on the basis of the defining equations (7) to (10) with the object of quantitative evaluation of the effects of various substituent groups on the reactivities of related series of compounds.

The slope of a $\log k$–$\log k$ plot is evidently equal by definition to the ratio of the Hammett ρ functions for the two series of reactions. The alternate term, "intrinsic reactivity," suggested recently[8] for the slopes of some $\log k$–$\log k$ plots may be misleading since relative ρ functions bear only an indirect and, in general, undefined relation to the reactivities of the attacking reagents.

Equations (7) to (10) do not consider temperature dependence of reaction rates, and the derived constants refer only to the particular temperatures of the two reaction series. If it is accepted that the temperature dependence of rate constants is adequately given by the Arrhenius equation

$$k_i=A_i\exp(-Ei/RT), \qquad (11)$$

then the condition for linearity of $\log k$–$\log k$ plots, Eq. (8), can be written in the form

$$S=\{[(E'_i-E'_j)/RT'] -\log(A'i/A'j)\}/\{[(E''_i-E''_j)/RT''] -\log(A''i/A''j)\} \qquad (12)$$

for any two of the homologous reactants (i, j). The substituent effect is now separated into its contribution to the activation energies and to the frequency factors. Equation (10) ought then to be written in the form

$$\log k_i'=\rho^{*\prime}[(\sigma^*_i/RT')+\gamma_i]+(m'/RT)+n' \qquad (13)$$

so that $-E'_i=\rho^{*\prime}\sigma_i^*+m'$ and $Ai=\exp(\rho^{*\prime}\gamma_i+n')$.

The constants m', n', $\rho^{*\prime}$, σ_i^*, and γ_i are now all temperature independent and the former three are constant for the series while the last two are characteristic for the particular reactant (i).

Three general types of reaction series ought then to be considered: the substituent effect results in an alteration of (1) activation energy only, (2) frequency factor only, and (3) both activation energy and the frequency factor. Provided both reaction series ($'$ and $''$) are of the same type, the respective linearity conditions for cases (1) and (2) become then

$$S\times(T'/T'')=(E_i'-E_j')/(E_i''-E_j'') \qquad (14a)$$

and

$$S=\log(A'_i/A_j')/\log(A_i''/A_j''). \qquad (14b)$$

The third case implies linear relationships between the activation energies and $\log A$, i.e.,

$$E_i'=\delta'\log A_i'+\beta'$$

so that

$$S=\frac{E_i'-E_j'}{E_i''-E_j''}\,\frac{(1/RT')+\delta'}{(1/RT'')+\delta''}. \qquad (14c)$$

The quantities β' and δ' are constant for the reaction series and depending on the sign of δ' there is a "compensating" or an "additive EA effect" on the rate constant. In addition to these three cases it is, in principle, also possible to have the two reaction series ($'$ and $''$) of two different types, giving thus additional three combinations (1:2, 1:3, and 2:3). The values of S for these cases can be readily deduced from the foregoing.

It is not possible to say whether examples of all of these different types of linear $\log k$–$\log k$ plots actually exist. The case of reaction series with constant A factors appears to be quite common.[9] The reactions of peracetic acid with olefins, which are of particular interest for the present work, belong into this class. This is shown in Table III, where some of the results of Böeseken and Stuurman[10] and of Böeseken and Hanegraaff[11] are given. The trend in the rate constants appears to be due entirely to variations in the activation energies. The deviation shown by cyclobutene and cyclopentene in contrast to cyclohexene and cycloheptene has been ascribed to the ring strain in the former two compounds.[10,11] The slope of the $\log k$–$\log k_0$ plot for these reactions, as shown in Fig. 3, is only about 2, although their rates are very much smaller (by a factor as large as about 10^{13}) and their activation energies are con-

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[8] M. Levy and M. Szwarc, J. Am. Chem. Soc. **77**, 1949 (1955); M. Szwarc, J. Phys. Chem. **61**, 40 (1957).

[9] Hinshelwood, Laidler, and Timm, J. Chem. Soc. 848 (1938).

[10] J. Böeseken and J. Stuurman, Rec. trav. chim. **56**, 1034 (1937).

[11] J. Böeseken and C. J. A. Hanegraaff, Rec. trav. chim. **61**, 69 (1942).

TABLE III. Rate constants, activation energies and A factors for some reactions of peracetic acid with olefins (determinations of Böeseken and Stuurman[10] and Böeseken and Hanegraaff.[11] Units: Moles per liter, minutes).

Olefin	$k_{(25.8°)}\times 10^3$	E kcal mole^{-1}	$\log_{10}A$
Ethylene	0.19	...	...
Propylene	4.2	...	...
n-Pentene-1	4.2	17.6	10.5
n-Hexene-1	4.8	17.4	10.4
Isobutene	92	15.6	10.4
Butene-2	93	...	...
n-Pentene-2	94	15.6	10.4
n-Hexene-2	99	15.3	10.2
n-Hexene-3	129	15.5	10.4
Trimethylethylene	1240	14.0	10.3
Cyclobutene	20.4	13.8	8.4
Cyclopentene	195	14.0	9.6
Cyclohexene	129	15.6	10.4
Cycloheptene	175	15.1	10.3

siderably larger than the likely values for the corresponding reactions of oxygen atoms. Inasmuch as the oxygen atom reactions are of the same type (constant A factors), the slope of 2 indicates only that identical structural changes of the olefins bring about twice as large increments in the activation energies of the peracetic acid reactions as in the corresponding oxygen reactions. Whether or not the series of oxygen atom reactions and of the other reactions of Fig. 3 possess constant A factors will have to be established by accurate determinations of the temperature coefficients of the rate constants. These are probably quite small[12] and their measurements will require high accuracy and relatively large temperature intervals. Inasmuch, however, as the reactions of the ground-state oxygen atoms and of the bromonium ions (the active species in the brominations), which are mutually isoelectronic, prove to be both with constant A factors, the slope of 0.65 shown in Fig. 3 would be brought to unity as a result of the difference in temperature [Eq. (14a)].

Analogous considerations apply to the linear plots of the type shown in Fig. 4. For example, if the reactions series has constant A factors, the condition for linearity is

$$\begin{aligned} E_i - E_j = RTS(Eexi - E_{exj}) &= RTS^*(I_i - I_j) \\ &= RTS^{**}(\Delta \mathrm{Hh}_i - \Delta \mathrm{Hh}_j) = \cdots \qquad (15) \end{aligned}$$

for any two of the homologous reactants (i, j). S, S^*, and S^{**} are the slopes of the respective plots. These relationships can, therefore, be expected to hold only when the increments in the activation energies caused by structural changes are proportional to the corresponding increments in some physical property of the homologous reactants. They have been utilized in the attempts to formulate a detailed mechanism of chemical reaction[13,8] in terms of the transition state theory.

Regardless of the physical significance of the slopes of the log$k$ plots, the linear correlations shown in Figs. 3 and 4, indicate that the trends in the rates of reactions of oxygen atoms, peracetic acid, Br_2, CBr_2 (and perhaps of ozone as well) with olefins and in some physical properties of the latter (ionization potentials, heats of hydrogenation, spectral excitation energies) are to a good approximation all determined by the same structural effects. These effects can be explained in terms of the electronic theory of organic reactions[14] as was done by Ingold and his co-workers[12] for the olefin bromination reactions and more recently by Swern[15] for the reactions of peracetic acid with olefins. It is assumed that the electron-releasing alkyl groups increase by induction the electron density of the double bond making it thus more susceptible to attack by electrophilic reactants. At the same time the plots in Fig. 4 show close correlations of logk_0 with some physical properties the trends in which have been ascribed partly to "hyperconjugation."[16–18] "Hyperconjugation," therefore, appears also to contribute to the structural factors which determine the rates of these reactions although the extent of that contribution is uncertain.

The rates of addition of oxygen atoms to propylene and butene-1 are very similar and the same is true for butene-2 and pentene-2. The contributions of a methyl and an ethyl group to the reactivity of the olefin are, therefore, about equal. At the same time both these alkyl groups exert strong orienting effects: in the case of propylene and butene-1 oxygen atoms add practically exclusively to the terminal carbon atom of the double bond, i.e., away from the alkyl radicals, as has been described in detail in the first part of this work.[2] On the other hand, in the case of pentene-2 oxygen atoms were found to add almost exclusively to the carbon atom to which CH_3 is attached and hardly at all to the carbon atom to which C_2H_5 is attached. If the same factors governed the rates and the position of addition, approximately equal addition to the two doubly bonded carbon atoms would be expected. This appears to suggest an initial interaction of oxygen atoms with the double bond as a whole, and only at a later stage, after the passage over the energy barrier (after the "activated complex" is formed) localization of oxygen atoms on one of the two carbon atoms of the original double bond. In agreement with this view a statistical factor of two does not have to be taken into account in the case of symmetrical olefins (including C_2H_4) in order to obtain the linear correlations shown. These correlations also seem to show that the

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[12] C. K. Ingold and E. H. Ingold, J. Chem. Soc. 2354 (1931); S. V. Anantakrishnan and C. K. Ingold, *ibid.* 984, 1396 (1935).

[13] R. A. Ogg, Jr., and M. Polanyi, Trans. Faraday Soc. **31**, 604 (1935); M. G. Evans and M. Polanyi, *ibid.* **34**, 11 (1938).

[14] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* (Cornell University Press, Ithaca, New York, 1953).

[15] D. Swern, J. Am. Chem. Soc. **69**, 1692 (1947).

[16] Mulliken, Ricke, and Brown, J. Am. Chem. Soc. **63**, 41 (1941);

[17] M. M. Kreevoy and H. Eyring, J. Am. Chem. Soc. **79**, 5121 (1957).

[18] R. W. Taft, Jr., and M. M. Kreevoy, J. Am. Chem. Soc. **79**, 4011 (1957).

rate constants depend on the structure of the olefins (the polarizability of the double bonds) rather than on the structure of any intermediates which are eventually formed. The configuration of the *activated complex* should not, therefore, be identified with the configuration of the *intermediates* which have to be postulated in order to explain the type of final products formed.

The nature of the transition complex and of the intermediates formed in olefin addition reactions has been the subject of considerable discussion and cannot be regarded yet as settled. General aspects of the subject have been treated, for example, by Wheland.[19] In the present discussion attention will be limited to some recent work directly related to the reactions considered here. Skell and Garner[6] suggest three-membered ring intermediates, i.e., simultaneous bond formation to both carbon atoms in the addition to olefins of some two electron deficient reagents, such as CBr_2, Br^+, peracetic acid (i.e., oxygen atoms derived from it). This appears to be supported by stereospecificity, for example, of some CBr_2 reactions, although the multiplicity of this molecule is uncertain. de la Mare and Pritchard,[20] on the other hand, in discussing recently some olefin chlorination reactions (addition of Cl^+), give some reasons against a three-membered ring intermediate and also argue that an "open" carbonium ion is a more likely intermediate than a π complex of the type suggested by Dewar.[21] In the reactions of oxygen atoms with olefins, as has been described in the first part of this work,[2] both the multiplicity of the ground-state oxygen atoms and the type of products formed require the formation of an "open" intermediate: a triplet biradical which allows rotation (though partially restricted) around the original double bond and partial rearrangement involving migration of groups. At the same time, as indicated in the foregoing, the activated complex is likely to be a stage in the interaction of oxygen atoms with the double bond as a whole. This implies an interaction between oxygen atoms and the double bond already at relatively large distances where the direct effect of substituents is still quite small. Under such conditions constancy of A factors would be favored as observed, for example, in the reactions of peracetic acid with various olefins. The subsequent formation of an intermediate will follow the energetically most favorable path within any spin conservation restrictions which may be imposed in specific cases.

The formation of final products from the intermediate involves in the case of ground-state (O^3P) oxygen atoms partial rotation about the original double bond and then both ring closure (epoxide formation) and migration of free radicals (including hydrogen atoms). The latter takes place always from the carbon atom to which oxygen atom is attached in the intermediate biradical to the other carbon atom of the original double bond.[2] These migrations are evidently necessitated in order that the carbonyl compounds can be formed and the nature of rearrangements and the energetic reasons for them are understandable. In this connection the stereospecificity of the reactions of $O(^1D)$ with olefins is of interest and there seems to be some experimental evidence that singlet oxygen atoms lead to an increased formation of epoxides and greater stereospecificity,[22] as would be expected.

The difference in the trends of rate constants of the two groups of reactions in Table II is of fundamental interest. In the terminology usually employed for classification of reagents in organic chemistry, it could be simply stated by saying that the first five are "electrophilic reagents" and the last three are "radical reagents."† The former are concerned with the electron-donating (nucleophilic) character of the olefinic double bonds, the latter with the free radical character of the olefins. Detailed formulations of the respective transition complexes would be at present quite uncertain. The electrophilic character of the ground-state oxygen atoms should be noted in spite of the fact that they do not possess a vacant orbital capable of forming a "dative" bond with the two π electrons of the olefin. The difference between the two classes of reagents perhaps reflects itself in a considerable variation in A factors in the mono-radical reactions, as has been recently discussed by James and Steacie[23] who have studied reactions of ethyl radicals with some olefins. This could then be ascribed to a weaker interaction between mono-radicals and olefinic double bonds (weak electrophilic character of the mono-radicals) and the consequent need for closer approach before the potential barrier can be overcome. However, there is evidently need for more extensive experimental information before definite conclusions can be drawn. It is hoped that it will be possible to discuss elsewhere certain aspects of these addition processes in the light of some molecular orbital calculations carried out in this Laboratory for a number of olefins.[22]

In the present work only relative values of the rate constants of addition of oxygen atoms to some olefins have been determined. The relative values can be obtained with considerable accuracy and are ideally suited for a number of purposes. At the same time it

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[19] G. W. Wheland, *Resonance in Organic Chemistry* (John Wiley & Sons, Inc., New York, 1955).

[20] P. B. D. de la Mare and J. G. Pritchard, J. Chem. Soc. 3990 (1954).

[21] M. J. S. Dewar, Nature **156**, 784 (1945); *ibid.* J. Chem. Soc. 406, 777 (1946); *ibid.*, Discussions Faraday Soc. **2**, 75 (1947).

[22] S. Sato and R. J. Cvetanović (to be published).

† See, for example, reference 19. The experimental information on ozone is limited and this compound is considered here only very tentatively, mainly with the object of stressing the need for further determinations of rate constants. In view of this, attempts are being made in this Laboratory to measure relative rate constants of reactions of ozone with some olefins in the vapor phase.

[23] D. G. L. James and E. W. R. Steacie, Proc. Roy. Soc. (London) **A244**, 297 (1958).

is of considerable interest to have some knowledge of the absolute values of these reactions and for this it is necessary to have a reliable absolute value for at least one of the reported reactions. In the preliminary communication[1] on the present work an attempt was made to obtain an approximate idea of the absolute values by using an earlier comparison of the rates of reactions of oxygen atoms with ethylene and *n*-butane and assuming a value of 10^{-5} for the collision yield of the latter reaction. This assumption was indirectly based on the classical experiments of Harteck and Kopsch[24] with pentane and hexane and was, of course, subject to large uncertainty. It is therefore worthwhile to summarize briefly some estimates of absolute values of these reactions now available. Recently a value of 1.9 was obtained in this Laboratory for the ratio of the rate constants of the reactions of ground-state oxygen atoms at 25° with NO_2 and butene-1 (this is considered a slightly more reliable value than the value obtained simultaneously for NO_2 and isobutene[4]). Ford and Endow[25] give 2.1×10^9 l mole^{-1} sec^{-1} for the rate constant of the reaction of oxygen atoms with NO_2 and this value lies within the limits found by Kistiakowsky and Kydd[26] (the collision yield $\geq10^{-2}$) and by Kaufman[27] (rate constant $\geq10^8$ l mole^{-1} sec^{-1}). One thus obtains 1.1×10^9 l mole^{-1} sec^{-1} for the rate constant of the reaction of oxygen atoms with butene-1 ($k_{\mathrm{Bu-1}}$). An approximate upper limit for $k_{\mathrm{Bu-1}}$ can be calculated by assuming that for the fastest reaction of oxygen atoms measured so far, that with tetramethylethylene, the collision yield is not greater than unity, i.e., that for this reaction approximately $k\leq6\times10^{10}$ l mole^{-1} sec^{-1}. This leads then to $k_{\mathrm{Bu-1}}\leq3.4\times10^9$ l mole^{-1} sec^{-1}. Ford and Endow,[28] with the use of a technique involving trace concentrations of reactants, obtained for the rate constant of the reaction of oxygen atoms with *cis*-pentene-2 1.1×10^{10} l mole^{-1} sec^{-1} which, in view of the relative rates reported here, gives $k_{\mathrm{Bu-1}}=3.0\times10^9$ l mole^{-1} sec^{-1}. Kaufman[27] finds an "over-all *k*" for the reaction of oxygen atoms with ethylene of about 5×10^7 l mole^{-1} sec^{-1}, which in view of the present relative values, gives $k_{\mathrm{Bu-1}}=3.1\times10^8$ l mole^{-1} sec^{-1}. Elias and Schiff[29] have obtained a tentative value of 1.2×10^7 l mole^{-1} sec^{-1} for the rate constant of the reaction of oxygen atoms with ethylene using a microcalorimetric method, which then gives $k_{\mathrm{Bu-1}}=0.74\times10^8$ l mole^{-1} sec^{-1}. A mean of 5×10^8 l mole^{-1} sec^{-1} is within a factor of seven consistent with all the quoted values for $k_{\mathrm{Bu-1}}$ derived from various sources. Evidently the uncertainty in the absolute values still remains quite appreciable, although the order of magnitude appears now to be well established.

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[24] P. Harteck and U. Kopsch, Z. physik. Chem. **B12**, 327 (1931).
[25] H. W. Ford and N. Endow, J. Chem. Phys. **27**, 1156 (1957).
[26] G. B. Kistiakowsky and P. H. Kydd, J. Am. Chem. Soc. **79**, 4825 (1957).
[27] F. Kaufman, J. Chem. Phys. **28**, 352 (1958).
[28] H. W. Ford and N. Endow, J. Chem. Phys. **27**, 1277 (1957).
[29] H. I. Schiff (private communication).