Rates of Reactions of Ozone with Chlorinated and Conjugated Olefins[1]

D. G. Williamson[2] and R. J. Cvetanović

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Abstract: The absolute values of the second-order rate constants for the reactions of ozone with chloroethylenes and allyl chloride have been determined in carbon tetrachloride solution at room temperature (25 ± 1°). The rate of ozone attack decreases strongly as the number of chlorine atoms in the olefin molecules is increased. The large variation in the values of the rate constants for the chloroethylenes, from 1.0 l. mole^{-1} sec^{-1} for C_2Cl_4 to 1200 l. mole^{-1} sec^{-1} for C_2H_3Cl, is believed to be primarily due to a predominantly electrophilic role of ozone in its reactions with these olefins. A pronounced additional trend is shown by the three isomeric dichloroethylenes: *trans*-1,2-$C_2H_2Cl_2$ is about 16 times more reactive than *cis*-1,2-$C_2H_2Cl_2$, while 1,1-$C_2H_2Cl_2$ is the least reactive of the three isomers. These trends are discussed in terms of the electronic and steric effects and are compared with the behavior of other 1,3 dipoles in their cycloadditions to olefins. Relative rates of ozonation of 1,3-C_4H_6 and styrene have been determined by competition with 1-pentene. The two conjugated olefins do not show a strongly increased reactivity and in this respect differ from the behavior reported for some other 1,3-dipolar cycloadditions.

Ozone appears to behave primarily as an electrophilic reagent in its reactions with aromatic compounds.[3] Excellent correlations have been found between the electron-donating properties of alkyl-substituted benzenes and their reaction rates with ozone in carbon tetrachloride solution.[4] Trends in the rates of ozone reactions with olefins have been studied to a considerably smaller extent. In an early study in this laboratory[5] a predominant electrophilic trend was indicated by the relative rates of ozonation of simple alkenes in the gas phase, although it was also necessary to invoke steric contributions and the dipolar character of ozone in order to explain some departures from simple correlations. We have confirmed this trend recently by measuring the relative and the absolute rates for the same reactions in carbon tetrachloride solution.[6] The reactions of alkenes are, however, much faster than those of the substituted benzenes, and the spread of values of rate constants is very small. A logical extension of the ozone–alkene investigations is to the halogen-substituted olefins, for which considerably larger differences in reaction rates may be expected because of stronger electronic interactions. The results which we have now obtained with the chlorinated ethylenes and allyl chloride confirm these expectations and are reported and discussed in the present article. For comparison with these results and the previous results with alkenes,[6] the rates of ozonation of the conjugated olefins 1,3-butadiene and styrene have also been determined.

Experimental Section

A simple stopped-flow apparatus was used to measure spectrophotometrically the rate of decay of ozone. A Beckman Model DU spectrophotometer was modified with an energy-recording adapter so that the signal output could be followed with a Hewlett-Packard Model 7100 strip chart recorder. The 100-mm long, 12-mm i.d. cylindrical optical cell (the reaction vessel) was firmly mounted inside the 100-mm cell compartment of the spectrophotometer so that the analyzing beam from the monochromator passed through the cell parallel to its cylindrical axis. The cell had a 3-mm i.d. inlet as close as possible to the front window and a similar exit tube as near as possible to the rear window. The reactant solutions were placed in two separate bottles and were pressurized with nitrogen gas which served to force the solutions into the mixing chamber and from there on into the cell. A 6-mm i.d. three-way spring loaded stopcock served as the mixing chamber. After the mixing chamber the solution passed through 10 cm of 6-mm i.d. tubing before entering the reaction cell. The nitrogen pressure over each solution was kept at about 10 psig, which gave a total flow of about 50 cm^3/sec through the reaction vessel. The time required to refill completely the cell with the mixed reaction solution was therefore only about 0.2 sec, which is much shorter than the reaction half-life of any reaction reported here. A steady-state concentration of ozone was attained after a very short time (about 0.2 sec after the flow was started). In all cases, immediately before the start of the reaction, the 100% transmission point was established with carbon tetrachloride pretreated in the manner described further below. After about 5 sec of flow at 50 cm^3/sec, the flow was stopped and the subsequent increase in per cent transmittance was measured as a function of time. Transmittance was monitored at 2800 Å where ϵ(ozone)[4] is 1670 M^{-1} cm^{-1}. Error due to the drift of the single beam spectrophotometer was negligible for the reaction times employed.

Ozone was generated by passing oxygen through a Tower Ozonizer which produced about 1–2% ozone in the oxygen. Baker Adamson reagent grade carbon tetrachloride was used as a solvent in all experiments. Ozone was found to decompose at a rate of about 30%/hr in this solvent at room temperature and so the following treatment was used in accordance with Nakagawa, Andrews, and Keefer.[4] Ozone was bubbled through the carbon tetrachloride in a wash bottle at room temperature for about 1 hr at 0.2 l./min. Nitrogen was then bubbled vigorously through the solvent several hours in order to displace the dissolved ozone. The solvent pretreated in this way proved satisfactory since ozone decomposed in it only at a rate of 2–3%/hr. No correction to the observed decay rates was necessary.

The following chlorinated olefins were used in the present experiments: Matheson, Coleman and Bell Spectroquality tetrachloroethylene, Baker Adamson Reagent Grade trichloroethylene, Eastman Kodak *trans*-1,2-dichloroethylene and *cis*-1,2-dichloroethylene, J. T. Baker 1,1-dichloroethylene, Matheson vinyl chloride, and Matheson Coleman and Bell allyl chloride. The *trans*-dichloroethylene contained about 13% of the *cis* isomer after one distillation but no other impurities detectable by mass spectrometric or gas chromatographic analysis. The *cis* isomer contained about 1–1.5% *trans* impurity. Butadiene-1,3 was Philips Research Grade, and styrene was an Eastman Kodak product used after vacuum distillation.

A Varian Model 90P gas chromatograph equipped with a gas

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[1] Issued as NRC Contribution No. 10241.

[2] National Research Council Postdoctorate Fellow.

[3] J. P. Wibaut and F. L. J. Sixma, *Rec. Trav. Chim.*, 71, 761 (1952).

[4] T. W. Nakagawa, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, 82, 269 (1960).

[5] T. Vrbaski and R. J. Cvetanović, *Can. J. Chem.*, 38, 1053 (1960).

[6] D. G. Williamson and R. J. Cvetanović, *J. Am. Chem. Soc.*, in press.

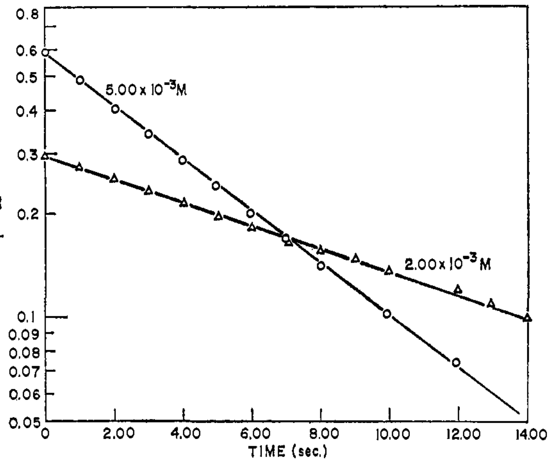

Figure 1. Kinetic plots for the reaction of ozone with *cis*-1,2-dichloroethylene (initial olefin concentrations: ○, 5.00 × 10^{-3} *M*; △, 2.00 × 10^{-3} *M*).

density detector and a 5-ft SE-30 silicone gum rubber on 60–80 firebrick column was used for stoichiometric determination and product analysis. Products were identified by their infrared spectra after separation by gas chromatography.

Results

In the absolute measurements of rate constants much larger concentrations of the chlorinated olefins than of ozone were used so that their concentrations remained effectively constant. The observed decay of ozone was therefore first order. A pseudo-first-order rate constant k' was determined from a plot of

$$\ln (A_t - A_\infty) = k't \quad (1)$$

where A_t and A_∞ are the light absorptions by ozone at time t and at infinite time, respectively. A_∞ was taken as the value of the absorption after several reaction half-lives. In all cases the value of A_∞ was less than or equal to 0.05 and did not drastically alter the decay curve, except in the range where the reaction neared completion. The second-order rate constant k is calculated from

$$k' = k[\text{olefin}] \quad (2)$$

No significant variation of k' outside of the likely experimental error of 5% around the mean value was found on changing the concentration of the chlorinated olefins.

Table I. The Second-Order Rate Constants (k) for the Reactions of Ozone with Olefins in CCl_4 Solutions at Room Temperature (25 ± 1°)

Olefin	k, l./mole sec
A. Chloroethylenes	
$CCl_2{=}CCl_2$	1.0
$CHCl{=}CCl_2$	3.6
$CH_2{=}CCl_2$	22.1
cis-$CHCl{=}CHCl$	35.7
trans-$CHCl{=}CHCl$	591
$CH_2{=}CHCl$	1,180
($CH_2{=}CH_2$	~25,000)[a]
B. Chloropropylene	
$CH_2ClCH{=}CH_2$	11,000
($CH_3CH{=}CH_2$	~80,000)[a]
C. Conjugated and Nonconjugated Alkenes	
1,3-Butadiene	74,000[b]
Styrene	103,000[b]
(Benzene	0.028)[c]
1-Pentene	81,000[d]
1-Hexene	76,000[d]
2-Hexene	148,000[d]
Isobutylene	97,000[d]
cis-2-Butene	163,000[d]
Trimethylethylene	167,000[d]
Tetramethylethylene	200,000[d]
Cyclopentene	200,000[d]

[a] These values are estimates based on experimental results for 1-hexene[6] and assuming that the relative rates for 1-hexene and ethylene and for 1-hexene and propylene[6,7] do not change much in going from the gas to liquid phase. [b] Determined in the present work using the competitive technique described in ref 6. [c] Taken from ref 4. [d] Earlier determination in this laboratory.[6]

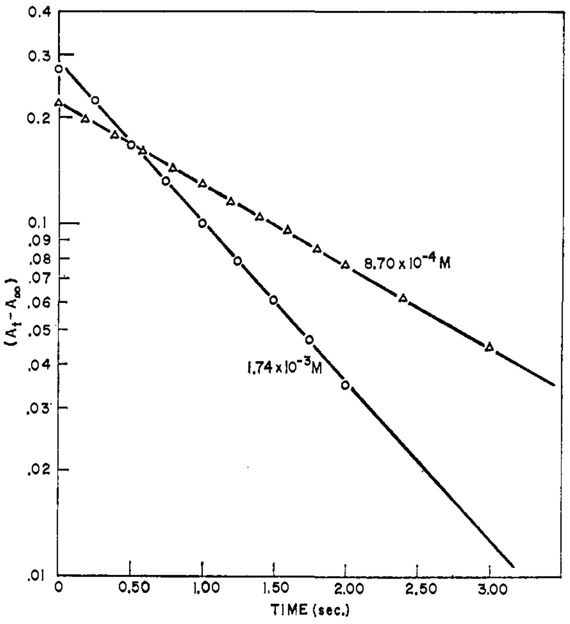

Figure 2. Kinetic plots for the reaction of ozone with *trans*-1,2-dichloroethylene (initial olefin concentrations: ○, 1.74 × 10^{-3} *M*; △, 8.70 × 10^{-4} *M*).

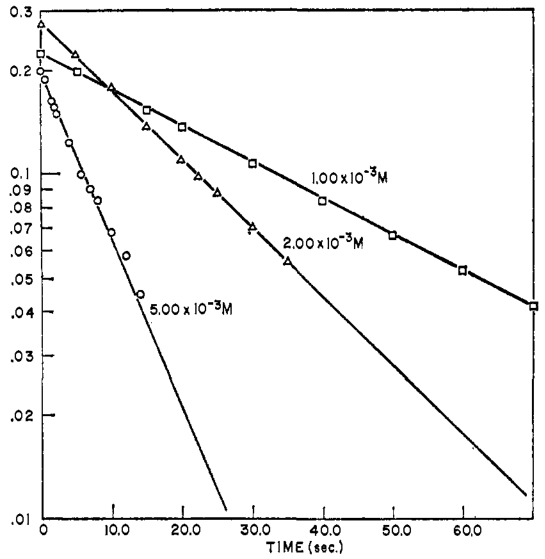

Figure 3. Kinetic plots for the reaction of ozone wth 1,1-dichloroethylene (initial olefin concentrations: ○, 5.00 × 10^{-3} *M*; △, 2.00 × 10^{-3} *M*; □, 1.00 × 10^{-3} *M*).

Examples of the first-order plots of the data are shown in Figures 1–3 for *cis*-1,2-dichloroethylene, *trans*-1,2-dichloroethylene, and 1,1-dichloroethylene, respectively. The values of the second-order rate constants at 25 ± 1° for the chlorinated ethylenes and for allyl chloride are shown in Table IA and B, respectively.

For 1,3-butadiene and styrene, relative rate constants were determined by competition with 1-pentene using the technique described earlier[6] and were converted to absolute values adopting for 1-pentene the value determined in the previous work.[6] Table IC gives the rate constants for 1,3-butadiene and styrene, and, for comparison, our earlier[6] values for several alkenes and the literature[4] value for benzene.

The stoichiometry of reaction of ozone with chlorinated ethylenes was determined for vinyl chloride, 1,1-dichloroethylene, and *cis*-1,2-dichloroethylene. A 10-ml portion of freshly ozonized CCl_4 solution was pipetted into 10.0 ml of a known concentration of the chlorinated ethylene dissolved in CCl_4. The ozone concentration was determined by titrating 10.0 ml of the same solution with $KI–Na_2S_2O_3$. Corrections were made to the titer of $Na_2S_2O_3$ to account for the reducible substances present in the CCl_4 after pretreating with O_3. Substrate concentrations were determined before and after reaction with O_3 using the gas chromatograph. A saturated hydrocarbon was used as internal standard. Concentrations in these experiments were typically 1.0×10^{-2} *M* in chlorinated ethylene and 3.0×10^{-3} *M* in O_3. The results are summarized in Table II. All experiments were done at room temperature. The last figure in each number is insignificant.

Table II. Stoichiometry of Some Ozone–$C_2H_{(4-n)}Cl_n$ Reactions

$C_2H_{(4-n)}Cl_n$	Moles of $C_2H_{(4-n)}Cl_n$ consumed/ mole of ozone added	Moles of $COCl_2$ formed/ mole of $C_2H_{(4-n)}Cl_n$ consumed
1,1-Dichloroethylene	1.05	1.0
cis-1,2-Dichloroethylene	0.98	0.18
Vinyl chloride	1.2	0.06

Phosgene was the only product readily detectable with gas chromatographic analysis. In the case of 1,1-dichloroethylene, phosgene was formed in nearly quantitative yields. A white solid compound was also found after the solvent was evaporated from a reacted solution. This white solid was probably peroxidic in nature since it exploded violently while it was being collected. No further attempt was made to isolate or further characterize higher molecular weight products. Table II shows phosgene yields from the reaction of the chlorinated ethylenes at concentrations of about 10^{-2} *M* with ozone solution at about 3×10^{-3} *M*. Yields were determined by the same method used in the stoichiometric experiments. Phosgene yields have been corrected for the small amount of phosgene formed from the reaction of ozone with the carbon tetrachloride solvent. This correction was large (about 50%) for the phosgene with vinyl chloride. When a 10^{-1} *M* solution of *cis*-dichloroethylene 50% reacted with ozonized oxygen, three other peaks whose relative areas changed with time were observed. Each had a shorter chromatographic retention time than $COCl_2$. These peaks were not observed when lower concentrations were used while determining the stoichiometry and phosgene yields.

Discussion

As in most of the earlier olefin ozonation work in this laboratory,[5–7] the main objective of the present kinetic investigation has been a determination of the rate constants. The data obtained can therefore provide information on the primary interaction between ozone and olefins, *i.e.*, on the transition state leading to the initial products (or intermediates), but not on the subsequent reactions of the initial products. The observed simple stoichiometry (Table II) indicates that the measured rate constants are those of the second-order attack of ozone on olefins, in agreement with the good second-order dependence observed in rate determinations. Although the product analysis in the present work has been incomplete, as is frequently the case in studies of this kind because of the analytical difficulties involved in the characterization of the peroxidic substances produced, there is strong indication that typical ozonolysis products are again formed.

The main contribution from the present and the earlier[5–7] kinetic studies is that they reveal at least a dual nature of the effect of olefin structure on the trends in reactivity. This is particularly well illustrated by the present data summarized in Table I. There is evidently a pronounced decrease in the rates of ozone attack on chloroethylenes (Table IA) as Cl is successively substituted for H. Such a behavior is consistent with a predominantly electron-demanding (electrophilic) character of ozone in its cycloaddition to these olefins since Cl is more electronegative than H and exerts an inductive electron-withdrawing effect reducing the electron density at the double bond. Although chlorine atoms exert both an inductive and an opposing mesomeric effect, it is reasonable to assume that the inductive electron withdrawal predominates. This conclusion is supported by the data in Table IB for propylene and allyl chloride, where again a chlorine substituent brings about a substantial decrease in reaction rate. In allyl chloride the Cl atom still exerts an inductive electron withdrawal but not a mesomeric electron donation to the double bond. The observed decrease in the rate must therefore be either due to the strong I^- effect of the chlorine atom or to a largely increased steric hindrance in going from a $CH_3\cdot$ to a $CH_2Cl\cdot$ group, with the former effect likely to be considerably more important. This is supported by the fact that 1-hexene and 1-pentene are both more reactive than allyl chloride and yet steric effects for the C_4H_9 and C_3H_7 should be as large as those for the CH_2Cl group, as indicated by the Taft's E_s value.[8] Taft's σ^* constants[8] show that Cl exhibits a strong I^- effect. At the same time, Table I also shows large differences in reactivity between the three dichloroethylene isomers, in which the inductive effects should be comparable. Clearly, an explanation based solely on an inductive electron withdrawal by chlorine atoms cannot be adequate.

In the previous kinetic studies in this laboratory[5,7] of the reactions of ozone with alkenes, it was already concluded[5] that the trend in reactivity could not be explained only in terms of an electrophilic attack by ozone, although this appeared to be the predominant

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(7) Y. K. Wei and R. J. Cvetanović, *Can. J. Chem.*, **41**, 913 (1963).

(8) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 556.

factor. An appreciably slower attack on 1,1-dialkylethylenes and on 1,3-butadiene than on 1,2-dialkylethylenes was observed, and this was interpreted to indicate a concurrent contribution of either or both of the following two additional effects: (1) steric hindrance by the bulky alkyl substituents, and (2) a dual role, *i.e.*, a dipolar character of ozone, exhibiting both an electrophilic and a nucleophilic tendency in the cycloaddition leading to the formation of the five-membered 1,2,3-trioxolane ring characteristic of the "initial ozonides."

Two explanations of the superposition of structural effects were considered possible,[5] involving either a two-step or a one-step initial attack. It is of course also possible that both a two-step and a one-step attack occur simultaneously (or even that there are two concurrent one-step attacks leading to different products). The formal reaction scheme is therefore

$$\text{olefin} + \text{O}_3 \xrightarrow{k_1} \text{product I}$$

$$\text{olefin} + \text{O}_3 \underset{k_{-c}}{\overset{k_c}{\rightleftarrows}} \text{(complex)}$$

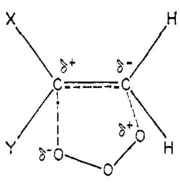
$$\text{(complex)} \xrightarrow{k_2} \text{product II}$$

so that the observed second-order rate constant (k) is

$$k = k_1 + k_2K_c/(1 + k_2/k_{-c}) \qquad (3)$$

where k_1 stands for the total rate of the one-step attack and $K_c = k_c/k_{-c}$. If $k_2 \ll k_{-c}$, $k \simeq k_1 + k_2K_c$. (Complex) is an olefin-ozone electron-donor acceptor complex susceptible to back-decomposition into the reactants. It can be a π complex or even a σ complex if it decomposes without geometric isomerization of the olefin. Product I may also be partly or wholly a complex but one which does not decompose back into the reactants. This distinction may not be trivial, although at the moment a choice between a one-step and a two-step mechanism is largely academic since there is no experimental information which would support unequivocally one of the two alternatives. To a large extent, however, the over-all effect of the substituents on the *observed* rate constants should be similar regardless of whether a two-step or a concerted one-step attack takes place.

The explanation suggested in the earlier work[5] for the dipolar role of ozone in its attack on the double bond of an olefin such as isobutylene or 1,3-butadiene was based on a transition state represented approximately by structure b. This was assumed to be formed *via* structure a through a cyclic shift of electrons either by rearrangement of a preequilibrated π complex or directly from the reactants in a concerted one-step attack. When X = Y = CH_3 (*i.e.*, isobutylene) or X = vinyl, Y = H (1,3-butadiene), the mesomeric delocalization of the partial positive charge, as in structure c, will decrease the stability of the transition state. (Some destabilization will be brought about by direct and indirect steric effects as well, as will be discussed further below, but at the moment attention is focused on electronic effects only.) Evidently, an analogous explanation can be proposed for the decreased reactivity of 1,1-dichloroethylene. A mesomeric delocalization of positive charge by Cl atoms is known[9] to lead to a substantial *decrease* in the ionization potentials of the chlorinated ethylenes although an opposite effect might have been expected *a priori*. Some mesomeric destabilization of the transition state may be expected for all chloroethylenes, and it is of interest that there is an approximate correlation between the rates of ozone attack on these olefins and their ionization potentials,[10] as shown in Figure 4, although there may be some uncertainty[11] in the ionization potential for *trans*-CHCl=CHCl. At first glance, the trend in Figure 4 could suggest a predominant nucleophilic role of ozone in these reactions. On the other hand, the mesomeric effect is absent in allyl chloride and its ionization potential (10.04 eV) is *larger* than that of propylene (9.73 eV), but the reaction rate is considerably *smaller*. The predominant role of ozone is therefore electrophilic. The reaction sequence shown by chloroethylenes (and other olefins) is, however, a result of superposition of (at least) two effects.



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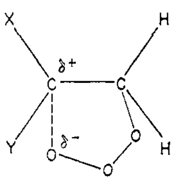

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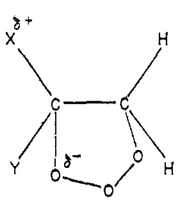

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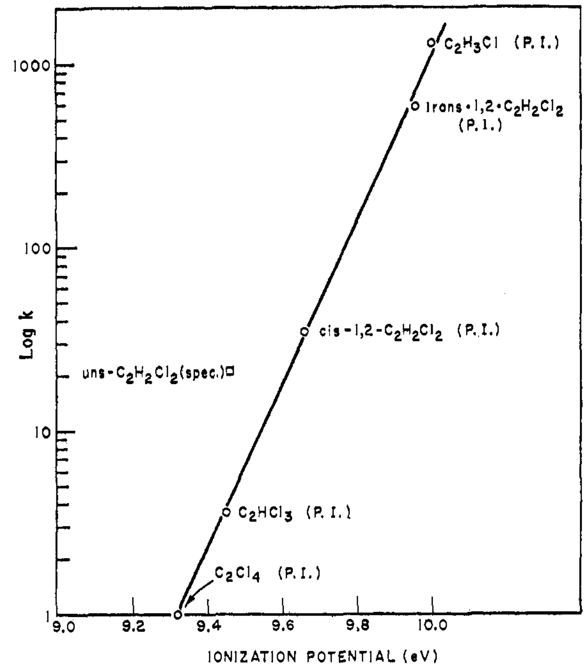

Figure 4. Plot of the logarithms of rate constants *vs.* the ionization potentials (taken from ref 10) of the chlorinated ethylenes. The method used in the determination of the ionization potential is indicated in brakets: P.I. = photoionization, spec. = vacuum ultraviolet spectroscopy.

Besides purely electronic effects, the potential influence of steric effects on the rates of olefin ozonation has been stressed in the earlier work from this laboratory.[5,7] Some of the decrease in reaction rates with increased substitution may be caused by *direct* steric hindrance to a close approach of the two reactants.

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[9] A. D. Walsh, *Trans. Faraday Soc.*, **41**, 35 (1945).

[10] R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall Inc., Englewood Cliffs, N. J., 1965, Appendix IV.

[11] A. D. Walsh and P. A. Warsop, *Trans. Faraday Soc.*, **63**, 524 (1967).

The steric hindrance may be particularly large for two substituents on the same carbon atom and could, for example, contribute to the low reactivities of isobutylene[5-7] and 1,1-dichloroethylene. An *indirect* steric effect may also play a role in 1,1-disubstituted ethylenes since the nonbonded repulsion between the two bulky substituents will increase as the sp^2 carbons assume some sp^3 character in the transition state.

The much lower reactivity toward ozone of *cis*-1,2-dichloroethylene than of the *trans* isomer is most probably due to indirect steric effects. A particular type of indirect steric effect has been invoked[12] to explain similar low reactivities of *cis*-1,2-disubstituted ethylenes in a number of dipolar cycloadditions to olefins. The two substituents and the two carbon atoms are believed to be constrained to remain in a plane in the transition state, and the nonbonded repulsion between the eclipsed substituents increases as the carbons assume some sp^3 character. An equivalent statement is that a departure from the eclipsed position (due to strong nonbonded repulsion) will affect adversely the ring closure in the transition state b by decreasing the overlap between the p orbitals of the carbon and oxygen atoms. Similar explanation may apply to the slow ozone reaction with *cis*-1,2-dichloroethylene. Our rough calculations show appreciably increased nonbonded repulsion between the two Cl atoms in the transition state, in agreement with large energy barriers to internal rotations in chloroethanes.[13] These calculations show also that the nonbonded repulsions between two chlorine atoms in the transition state are considerably smaller in 1,1- than in *cis*-1,2-dichloroethylene, although the former is the less reactive of the two. An important influence of other factors is therefore indicated, such as electronic and direct steric effects, as already mentioned, though the very approximate nature of these calculations must be stressed again. A quantitative evaluation of the contributions of the various factors which influence the reaction rates would hardly be feasible at present.

The dipolar character of ozone and of a number of related reagents in their addition to olefins has been recently discussed by Huisgen,[12] after a collective classification of these reactions as "1,3-dipolar cycloadditions." A concerted one-step attack and a development of both an electrophilic and a nucleophilic tendency in the "dipoles," with resultant cyclic electron shift in the transition state, are assumed. In the case of ozone, these postulates are similar to those discussed above, with the questions of a possible preequilibrated complex formation, the extent of simultaneity in the formation of the two C–O bonds, and the extent of charge development and separation in the transition state left largely open. Some of the generalized observations in the "1,3-dipolar cycloadditions" which can be compared with the present results are that (1) conjugated olefins show a pronounced increase in reactivity, (2) *cis* isomers of the 1,2-disubstituted ethylenes react much more slowly than the *trans* isomers, and (3) chlorinated alkenes react especially poorly. The present data evidently agree very well with points 2 and 3. On the other hand, the information now available on conjugated olefins appears to be in conflict with point 1. Thus, for example, the data in Table I show that both 1,3-butadiene and styrene react more slowly than 2-butene. Intuitively, the opposite might perhaps have been anticipated. A slowing down of the ring-closing step through positive charge delocalization, as discussed above, provides a potential explanation.

In the earlier study of the products of reactions of ozone with a number of simple alkenes in the gas phase,[14] we have observed in some cases not only the usual ozonolysis products but also small amounts of products formed by transfer of an oxygen atom from ozone to the olefins (*e.g.*, acetaldehyde from C_2H_4, propanal from C_3H_6, 1-butanal from 1-C_4H_8, isobutyraldehyde from *i*-C_4H_8). These results, interpreted in terms of a loss of O_2 from an intermediate σ-complex, suggested two types of ozone attack on olefins: ozonolysis and oxygen transfer. Many examples of the latter type of interaction have been quoted in the literature.[15,16] A systematic study of the relative importance of the two interactions has been recently carried out by Bailey and Lane[16] for olefins of the type $RR'C{=}CH_2$. They have found that oxygen transfer becomes more important (and is sometimes the predominant process) as the R and R′ substituents become bulkier. These results were explained on the basis of a competition between two distinct processes: (a) a purely electrophilic ozone attack, involved in the oxygen-transfer process (*i.e.*, formation of a π and/or σ complex followed by loss of O_2), and (2) a concerted 1,3-dipolar cycloaddition, involved in the "ozonolysis" (*i.e.*, formation of an "initial ozonide"). In the earlier and the present work we have observed largely "electrophilic" trends in the rates of ozone attack on olefins, indicating a predominantly electron-demanding tendency of ozone in these reactions, although ozonolysis is almost the only process and at best only very little oxygen transfer occurs. These results need not be taken to be in conflict with the views of Bailey and Lane since both the stability of the complexes which may precede the dipolar cycloaddition and the magnitudes of the rates of the dipolar cycloaddition itself should be largely determined by the electron-donating ability of the olefins. The electrophilic tendency of ozone may therefore play a dominant role not only in the oxygen-transfer reaction but in ozonolysis as well; the observed trends in reaction rates appear to show that this is indeed so.

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(12) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 633, 565 (1963).

(13) T. D. Alger, H. S. Gutowsky, and R. L. Vold, *J. Chem. Phys.*, **47**, 3130 (1967).

(14) T. Vrbaski and R. J. Cvetanović, *Can. J. Chem.*, **38**, 1063 (1960).

(15) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(16) P. S. Bailey and A. G. Lane, *J. Am. Chem. Soc.*, **89**, 4473 (1967)