A Quantitative Investigation of the Ozonolysis Reaction. X. On the Kinetics of the Reaction of Ozone with Ring-Substituted Styrenes in Carbon Tetrachloride Solution[1]

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Abstract: The specific rate constants for the reaction of ozone with olefins have been determined for ring-substituted styrenes in carbon tetrachloride solution at temperatures between 5 and 35°. The second-order rate constants obey Hammett's equation $\log k = \log k_0 + \rho\sigma$. The negative value of ρ (-0.91 ± 0.03) indicates that the ozone attack is electrophilic in nature.

Ozonolysis is frequently used in the determination of the structure of organic molecules. However, for molecules containing several carbon–carbon double bonds, relatively little is known about the preferential sites of ozone attack. Both electronic and steric factors related to the substituents on the carbon atoms forming the double bond are likely to influence the course of the ozonolysis. A knowledge of the kinetic data for the ozone attack on carbon–carbon double bonds may prove helpful for discussing the preferential sites of attack. In addition, evidence for the mode of attack of ozone can be gained from kinetic data.

Early qualitative investigations by van Dijk[2] on the relative rates of ozonization of methyl derivatives of benzene indicated that the introduction of methyl groups enhances the reactivity of the benzene ring toward ozone attack. Subsequent work on the methylbenzenes by Wibaut, *et al.*,[3-5] confirmed these observations and they showed that electron-withdrawing groups, such as the halogens and the carboxyl group, substituted on the benzene ring or on side chains (for example, the α-halogenotoluenes) reduce the rate of reaction between ozone and the benzene ring. On the basis of these observations, it was concluded[3,4] that the reaction between ozone and the substituted benzene rings takes place *via* an electrophilic ozone attack. This view appears to be confirmed by the observation[3,5] that catalysts such as aluminium chloride, ferric chloride, and boron trifluoride, all of which promote attacks by electrophiles, enhance the rate of reaction between ozone and the benzene derivatives. This is not at variance with the evidence that the ozone–olefin reaction is usually a 1,3-dipolar cycloaddition.

More recent studies by Nakagawa, *et al.*,[6] on the kinetics of ozonization of polyalkylbenzenes, in CCl_4 and CH_3COOH solution, indicate that the logarithms of the rate constants for the ozonolysis of polymethylbenzenes increase linearly with the number of methyl substituents on the aromatic nucleus. The rate constants for the polyethyl- and polyisopropylbenzenes are similar in magnitude to those for the polymethylbenzenes, with the exception of hexaethylbenzene which is explained on steric considerations. These results therefore confirm the interpretation of the ozone attack on carbon–carbon double bonds in terms of an electrophilic attack.

Similar conclusions are also drawn by Cvetanović, *et al.*, from their results of ozonization of alkenes in the gas phase[7] and in CCl_4 solution.[8] However, in order to explain the departures from simple correlations, in some cases steric effects and the dipolar character of ozone had to be invoked. The rate constants for the ozonolysis of chloroethylenes and allyl chloride, in CCl_4 solution, indicate[9] that the rate of ozone attack decreases rapidly as the number of chlorine atoms in the olefin molecules is increased. The values of the measured rate constants, which are discussed in terms of electronic and steric effects, thus confirm the predominant electrophilic role of ozone in its reactions with olefins.

It is considered that the trends in the rates of ozonolysis of simple olefins require further examination. The object of the present work is to obtain kinetic data on the reaction of ozone with ring-substituted styrenes, in carbon tetrachloride solution. The ring-substituted styrenes were used for two reasons: (i) the products of the ozone attack are well established, as explained below; and (ii) no steric effects interfere with the comparison of the rate constants measured for the different olefins and, thus, the electronic contributions can be discussed in isolation.

Experimental Section

Materials. The olefins (K & K Laboratories, Inc., and Aldrich Chemical Co., Inc.) were used without further purification. Gas chromatographic analyses indicated that the substances used were pure. Carbon tetrachloride, freshly distilled in an Ilas column, Todd type, was further treated to prevent the rapid decomposition of ozone (about 40% per hr) caused by impurities in the CCl_4. A treatment similar to that indicated in ref 4 was employed. A stream of ozonized oxygen was bubbled through the carbon tetrachloride at a rate of about 15 mmol of O_3/hr at room temperature for 45 min, when the solution became pale blue and smelled strongly of O_3. The ozonated solution was then flushed with a stream of dry nitrogen for 2-3 hr until the emergent N_2 gas contained no ozone as indicated by its inability to free iodine from an aqueous solution of KI. This carbon tetrachloride was suitable for kinetic measurements. Ozone was delivered to the pretreated solvent at a flow rate of 15 mmol/hr to give an approximately 10^{-3} *M* solution of O_3 in CCl_4.

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[1] Paper IX: *Can. J. Chem.*, in press.

[2] J. van Dijk, *Rec. Trav. Chim. Pays-Bas*, **67**, 945 (1948).

[3] J. P. Wibaut, F. L. J. Sixma, L. W. F. Kampschmidt, and H. Boer, *ibid.*, **69**, 1355 (1950).

[4] J. P. Wibaut and F. L. J. Sixma, *ibid.*, **71**, 761 (1952).

[5] F. L. J. Sixma, H. Boer, and J. P. Wibaut, *ibid.*, **70**, 1005 (1951).

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

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

[8] D. G. Williamson and R. J. Cvetanović, *J. Amer. Chem. Soc.*, **90**, 3668 (1968).

[9] D. G. Williamson and R. J. Cvetanović, *ibid.*, **90**, 4248 (1968).

The olefin solutions (approximately 1.5×10^{-2} *M*) were prepared by dissolving known quantities of olefin in 50 ml of pretreated CCl_4. The solutions were stored cold and used within 1 week of preparation.

Kinetic Measurements. The ozone and olefin solutions were brought to the temperature required. These temperatures were 5 ±0.1, 15 ± 0.1, 25 ± 0.1, and 35 ± 0.1°. A known quantity of ozone solution was transferred to one of the matching set of uv 1-cm spectrophotometer cells. The ozone solution and a blank were placed in the thermostated cell holder of a Bausch and Lomb Spectronic 505 spectrophotometer and allowed to equilibrate to the temperature of the housing. Absorption spectra between 270 and 310 mμ were taken at 10-min intervals to measure any change in the spectrum resulting from ozone decomposition in the solution. A decomposition of ozone of 3-4% per hr at 25° was observed. This decomposition could not be prevented by pretreatment of the solvent. However the decomposition did not significantly affect subsequent kinetic measurements.

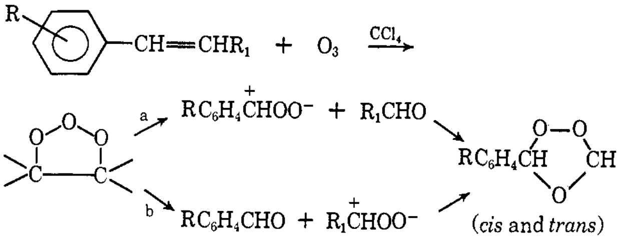
The required quantity (5 μl) of olefin solution sufficient to give an approximate 10^{-4} *M* solution was added to the cell containing the ozone solution by means of a microsyringe. The cell was shaken rapidly and the absorption spectrum between 270 and 310 mμ taken at specific time intervals. The spectra indicated the decrease in ozone concentration due to its reaction with the olefin. The change in optical density at 280 mμ was noted and the ozone concentration calculated assuming an extinction coefficient of 1670 M^{-1} cm^{-1}, as determined by Nakagawa, *et al.*[6] Control experiments indicated that the extinction coefficients of olefin and possible products (namely the appropriate aldehydes and ozonides) were small at 280 mμ and hence did not contribute to the absorption spectrum. The rate constants were determined a minimum of 7-12 times and are expressed (Table IV) with a 95% confidence limit.

The gas chromatographic analyses were made using a 5750 F & M gas chromatograph, using a flame detector. Six-foot columns of 10% Hyprose on Chromosorb P and of silicone rubber UC W 98 were used. The chromatograms were integrated by means of a planimeter and the area under the peak corresponding to the olefin which did not react was compared to the areas under the peaks obtained under the same conditions using standard solutions of the olefin. The analyses were repeated a minimum of 5 times. The reproducibility is within 2%. The ratios reported in Table I are accurate within 7%, accounting for errors in initial and final ozone and styrene concentration measurements.

Results and Discussion

Reaction Products. Stoichiometry. The ozonolysis of styrene and of ring- and β-substituted styrenes has been the object of recent studies.[10] It has been well established, for these olefins, that their ozonolysis proceeds according to the Criegee mechanism,[11] with the possible participation of *syn* and *anti* zwitterions following Bailey's scheme.[12] The evidence includes ^{18}O-labeling experiments[13] and measurements of ozonide *cis–trans* ratios.[13,14]

Scheme I



All the reaction products (in carbon tetrachloride solution) have been identified, *i.e.*, the normal and the cross ozonides, and the two aldehydes. In addition, some peroxidic material is also produced from the reaction between zwitterions. However, zwitterions can also be involved in a reaction which results in a mutual reduction[15] to yield aldehyde and oxygen. It is therefore difficult to determine, with accuracy, the stoichiometry of the reaction between ozone and olefin on the basis of analyses of the products formed in CCl_4 solution.

In the presence of methanol (1 *M* in CCl_4), however, the zwitterions are quantitatively trapped to form α-methoxy hydroperoxides, which do not react further with the aldehydes also formed during the ozonolysis.[10,16] In a number of cases it has been shown[10] that 1 mol of aldehyde mixture is formed by ozonolysis of 1 mol of olefin. In addition, the iodometric determination of the methoxy hydroperoxide indicated that a total of 1 mol of methoxy hydroperoxide is formed per mol of olefin used.[10] More recent polarographic analyses[18] of the reaction products obtained in the presence of methanol also confirmed that the ozonolysis of 1 mol of olefin produces 1 mol of methoxy hydroperoxide mixture. These observations imply that the ozone–olefin reaction proceeds with a 1:1 stoichiometry, as indicated in Scheme I.

Since the stoichiometry of the ozone–olefin reaction plays a crucial role in defining its kinetic expression, it is considered that additional evidence for this stoichiometry is desirable. Styrene solutions were allowed to react with less than the equivalent amount of ozone until they had reacted completely (about 30 min). The solutions were then analyzed for the unreacted olefin (Table I) by gas chromatography. In two cases, the reaction mixtures were analyzed before complete consumption of ozone, but when the rate of reaction was sufficiently slow to permit accurate analysis.

Table I. Stoichiometry of the Ozone–Styrene Reaction in CCl_4

Ozone concentration, $\times 10^4$ *M*		Styrene concentration, $\times 10^4$ *M*		$\frac{\text{Ozone used}}{\text{Styrene used}}$
Initial	Final	Initial	Final	
2.7	0.0	3.0	0.45	1.05
5.4	0.0	6.0	0.40	0.96
4.2	0.0	9.3	4.9	0.95
3.0	0.9	3.6	1.55	1.03
3.5	1.1	3.0	0.75	1.07

These direct experiments confirm the 1:1 stoichiometry of the olefin–ozone reaction, *i.e.*, 1 ozone molecule for each double bond. This result agrees thus with those previously reported for 1-hexene,[8] chlorinated ethylenes,[9] and polyalkylbenzenes,[2–4] although, for the latter compounds, only indirect evidence could be presented for the stoichiometry of the reaction. This

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(10) S. Fliszár, *Can. J. Chem.*, **44**, 2351 (1966); S. Fliszár and J. Renard, *ibid.*, **45**, 533 (1967); S. Fliszár and M. Granger, *J. Amer. Chem. Soc.*, **91**, 3330 (1969).

(11) R. Criegee and G. Wenner, *Ann.*, **564**, 9 (1949); R. Criegee, *ibid.*, **583**, 1 (1953); R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).

(12) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Amer. Chem. Soc.*, 90, 1822 (1968).

(13) S. Fliszár and J. Carles, *ibid.*, **91**, 2637 (1969).

(14) S. Fliszár and J. Carles, Preprints of Papers, Division of Petroleum Chemistry, American Chemical Society, Minneapolis, Minn., April 13-18, 1969, p A59; ref 1.

(15) S. Fliszár and J. B. Chylińska, *ibid.*, **46**, 783 (1968).

(16) Kolsaker and Bailey[17] have shown that methoxyhydroperoxides react with aldehydes in Baeyer-Villiger fashion when the reaction mixtures are allowed to stand for several days at room temperature, and when they are heated to reflux until the peroxide is decomposed. It is important, therefore, to analyze for aldehyde immediately. However, control analyses performed 2 hr after the ozonolysis did not indicate any appreciable change in the aldehyde content.

(17) P. Kolsaker and P. S. Bailey, *Acta Chem. Scand.*, 21, 537 (1967).

(18) J. Renard and S. Fliszár, *Can. J. Chem.*, **47**, 3333 (1969).

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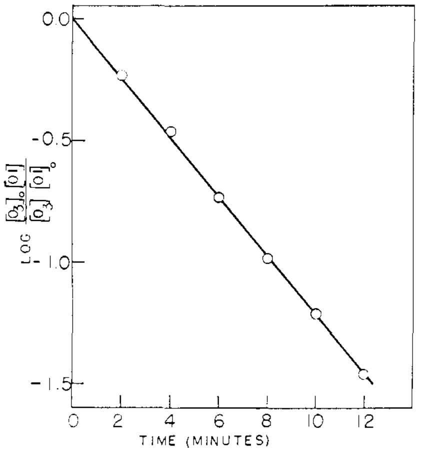

Figure 1. A typical example of the kinetic plot for the ozone–olefin reaction.

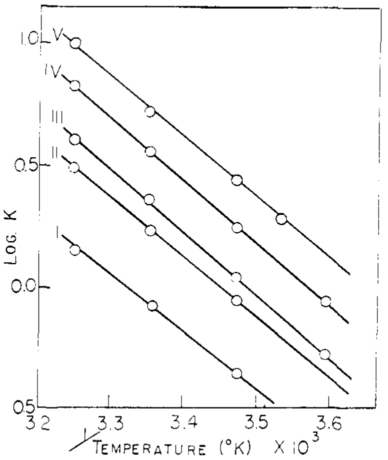

Figure 2. Arrhenius plots for the reaction of ozone with various olefins in CCl_4 solution: I, *m*-nitrostyrene; II, *m*-chlorostyrene; III, *p*-chlorostyrene; IV, styrene; V, *p*-methylstyrene.

strong evidence for a 1:1 stoichiometry in the ozone–olefin reactions indicates that the phenyl ring is not appreciably attacked by the ozone under the present experimental conditions. The results of Nakagawa, *et al.*,[6] showed that the rate constant for the ozone–benzene reaction is 0.028 M^{-1} sec^{-1} in carbon tetrachloride at 25.2°. This value is approximately one-hundredth of that measured in the present experiments and hence an ozone attack on the phenyl group of the substituted styrenes is unlikely to affect the measured kinetic values to any significant extent.

Rate Constants. On the basis of the evidence that the ozone–olefin reaction takes place with a 1:1 stoichiometry, the consumption of olefin may be deduced from the consumption of ozone as follows

$$[\mathrm{Ol}] = [\mathrm{Ol}]_0 - ([\mathrm{O_3}]_0 - [\mathrm{O_3}]) \qquad (1)$$

where [Ol] and $[\mathrm{Ol}]_0$ represent the olefin concentrations at time $t = t$ and $t = 0$, respectively, and $[\mathrm{O_3}]$ and $[\mathrm{O_3}]_0$ the ozone concentrations at time $t = t$ and $t = 0$.

Assuming a bimolecular reaction between ozone and olefin, the consumption of ozone may be written

$$-\mathrm{d}[\mathrm{O_3}]/\mathrm{d}t = k[\mathrm{Ol}][\mathrm{O_3}] \qquad (2)$$

and the integral rate law as

$$\log([\mathrm{Ol}][\mathrm{O_3}]_0/[\mathrm{O_3}][\mathrm{Ol}]_0) = kt([\mathrm{Ol}]_0 - [\mathrm{O_3}]_0)/2.3 \qquad (3)$$

provided that $[\mathrm{O_3}]_0 \neq [\mathrm{Ol}]_0$. A plot of the logarithms in eq 3 *vs.* t enables k to be calculated from the slope of the straight line and the initial ozone and olefin concentrations. A typical example of such a kinetic plot is given in Figure 1.

It is noteworthy that the agreement of eq 3 with the experimental results, as indicated in Figure 1, confirms the order of reaction postulated in eq 2. Attempts to calculate the rate constants, made with the assumption of orders of reaction different from unity (referred to each reactant), failed in giving constant values for k.

Table II is an example of two typical runs, made with styrene, from which k is calculated by means of eq 3 and 1.

For each olefin, at the appropriate temperature, the rate constants have been determined from 7 to 12 independent runs. The k values indicated in Table III illustrate the reproducibility of the rate measurements.

Table IV presents a summary of the experimental results. The indicated rate constants, k (M^{-1} sec^{-1}), are expressed with a 95% confidence limit.

Table II. The Ozonolysis of Styrene in CCl_4 at 25 ± 0.1°

Run	Time, sec	[Ol] × 10⁴, *M*	[O₃] × 10⁴, *M*	*k*, M^{-1} sec^{-1}
1	0	2.90	3.90	
	120	2.50	3.50	3.66
	240	2.18	3.18	3.52
	360	1.94	2.94	3.45
	480	1.70	2.70	3.54
	600	1.52	2.52	3.54
	720	1.34	2.34	3.67
			Mean	3.56
2	0	1.75	4.75	
	120	1.45	4.45	3.50
	240	1.20	4.20	3.55
	360	0.97	3.97	3.80
	480	0.85	3.85	3.56
	600	0.70	3.70	3.71
	720	0.60	3.60	3.68
			Mean	3.63

Table III. Rate Constants, *k*, Determined for *m*-Nitrostyrene in CCl_4 at 25 ± 0.1°

[Ol]₀ × 10⁴, *M*	[O₃]₀ × 10⁴, *M*	*k*, M^{-1} sec^{-1}
3.58	6.0	0.80
2.24	6.1	0.78
2.24	6.0	0.87
2.24	5.4	0.87
2.24	5.2	0.90
1.50	4.7	0.85
1.20	3.2	0.82
	Mean	0.84

Satisfactory Arrhenius plots were obtained for log k *vs.* $1/T$ (Figure 2), which permitted the calculation of the experimental activation energy. The values calculated for the activation energies were 11.42 (R = CH_3), 11.65 (R = H), 11.65 (R = *p*-Cl), 11.42 (R = *m*-Cl), and 11.20 kcal/mol (R = *m*-NO_2). All these values are thus, as expected, lower than the activation energies determined by Nakagawa, *et al.*,[6] for the ozone reaction with polyalkylbenzenes in carbon tetrachloride

Table IV. Rate Constants for the Reaction of Ozone with Olefins $RC_6H_4CH{=}CH_2$ in Carbon Tetrachloride Solution

R	Temp, °C ± 0.1° 5	15	25	35
p-CH_3	1.32 ± 0.15	2.81 ± 0.53	5.29 ± 0.37	10.00 ± 1.30
H	0.90 ± 0.05	1.74 ± 0.10	3.64 ± 0.36	6.65 ± 0.90
p-Cl	0.52 ± 0.05	1.09 ± 0.16	2.25 ± 0.22	3.98 ± 0.58
m-Cl	0.41 ± 0.04	0.87 ± 0.10	1.70 ± 0.19	3.14 ± 0.28
m-NO_2	*a*	0.44 ± 0.07	0.84 ± 0.06	1.39 ± 0.15

[a] Rate constant too low to be determined.

solution (approximately 13.0 kcal/mol). Owing to the experimental limitations, it was not possible to show a distinct trend of decreasing activation energies for the more electron-releasing substituent group in the ring-substituted styrenes.

Due to the uncertainties of the values for the activation energies, the entropy change accompanying the ozone attack can only be given as a rough approximation. The value of 18.4 ± 1.8 eu which can be calculated for all the olefins from the data presented in Table IV is similar to the value determined (21 ± 2 eu) for the polyalkylbenzenes in carbon tetrachloride solution.

The influence of the ring substituents on the rate constants can easily be interpreted in terms of Hammett's relationship 4[19] where k_0 is the rate constant for styrene.

$$\log k = \log k_0 + \rho\sigma \qquad (4)$$

Figure 3 indicates that the experimental results presented in Table IV are satisfactorily represented by eq 4, with $\rho = -0.91 \pm 0.03$. The slopes of the Hammett plots, *i.e.*, ρ, do not appear to differ significantly at temperatures between 5 and 35°. However, because of the uncertainties due to experimental limitations in the measurements of k, it should not be inferred, from these data, that the ρ values are necessarily independent of temperature.[20]

However, the satisfactory agreement of eq 4 with the experimental k values indicates, unambiguously, that electron-releasing substituents favor ozone attack on the carbon–carbon double bond, whereas electron-withdrawing substituents result in a lowering of the rate constant and hence reduce the possibility of ozone attack. It may thus be concluded that the ozone attack takes place according to an electrophilic process.

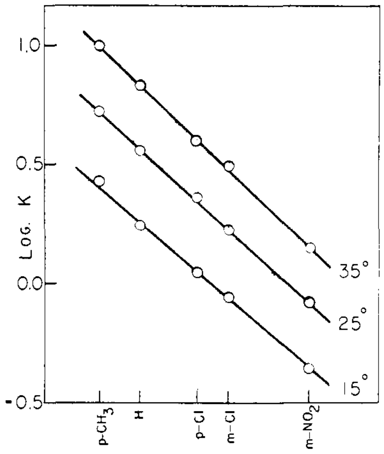

Figure 3. Variation of log k with Hammett's substituent constants at various temperatures.

Acknowledgment. The financial support given by the National Research Council of Canada is gratefully acknowledged.

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[19] L. P. Hammett, *J. Amer. Chem. Soc.*, **59**, 96 (1937); *Trans. Faraday Soc.*, **34**, 156 (1938); "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

[20] It appears nevertheless that ρ is not inversely proportional to T as anticipated by Hammett's ρ–T interrelationship.

Reactions of Dichlorocarbene with Olefins. Temperature Dependence of Relative Reactivities

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Abstract: Relative rates of addition of CCl_2 to olefins were determined between 0 and −80°. Relative olefin reactivities were found to vary with temperature, but were independent of the method of CCl_2 generation. Activation parameters were determined for the addition reaction. The olefin–CCl_2 addition mechanism and the relation of CCl_2 to other electrophilic species are discussed.

The chemistry of dichlorocarbene has had much attention during the past 15 years. Methods are available for generation of this carbene over the temperature range −100 to 1500°. Nonetheless reports of the effect of temperature on this (and other) carbene reactions are scarce. It was of interest to learn if activation