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CONTRIBUTION TO THE KINETICS OF OZONE–OLEFIN REACTIONS

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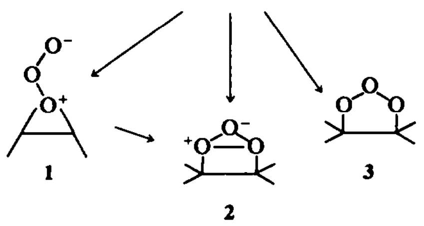
Abstract—Kinetics of the reaction of O_3 with single olefins and olefin-pairs have been investigated. The reactions were carried out by passing O_3 into a solution of the olefin(s). Most relative rate data gave the best fit to a zero order rate law, especially in cases where olefin consumption was extensive. The results are interpreted in terms of a reversible complex.

INTRODUCTION

In recent years there has been considerable interest in the kinetics and mechanistic details of the reaction of ozone with olefins. Experimental conditions used by Cvetanovic[1,2] and Flizlar[3] insured that the reactions were either second order or pseudo-first order, i.e. reactions using ozone in solutions generally were performed in the presence of a large excess of olefin. Cvetanovic[2] postulated a multistep-mechanism with formation of an undefined complex, i.e. a π-complex or a σ-complex, preceding C—C-bond cleavage. Most of these studies can be reconciled with the 1,3-dipolar addition concept.[4]

Studies by Story[5] based on ozonolysis of olefin solutions in the presence of aldehydes appear to be inconsistent with the 1,3-dipolar addition concept. Instead, a σ-complex, 1, has been postulated; followed by interconversion to the Staudinger molozonide, 2. Heicklen *et al.*[6] have cautioned against the extensive invocation of intermediates en route to the primary ozonide, 3, based on their low temperature IR studies.



The type of reaction where ozone in a carrier gas stream is bubbled into the solution of an organic compound whose extensive or complete conversion is desired is still of considerable practical interest and importance, however; be it for reasons of synthesis, analytical determination, or pollution control. For this type of reaction early data by Noller[7] indicated a clear difference in reactivity between *cis*- and *trans*-olefins. Wagner[8] and Greiner[9] showed that passage of ozone into an olefin gave zero order kinetics, but that the rate of disappearance was structure dependent. Competition experiments using two olefins have not been carried out in this fashion.

A simple analysis suggests a competition between two olefins when ozone is passed into a solution of such olefins

$$O_3 + trans \xrightarrow{k_1} \text{Products}_1$$

$$O_3 + cis \xrightarrow{k_2} \text{Products}_2$$

$$\frac{d\,trans}{d\,cis} = \frac{k_{1(trans)}}{k_{2(cis)}} = \log \frac{trans_f/trans_i}{cis_f/cis_i}$$

where f and i refer to initial and final concentrations of the respective isomers. This analysis was used by Cvetanovic[1] in his determination of relative rate constants using olefin and ozone solutions, where the olefin was present in large excess.

Fig 1, a log–log plot of the disappearance of 2-octene and stilbene isomers shows that there are cases where this analysis is followed over a wide concentration range. On the other hand, further investigation[10] showed that this case was not general and did not hold for many other olefin isomer pairs nor two different olefins, and especially did not hold when olefin consumption was extensive. For this reason we also decided to measure the rate of disappearance of some single olefins.

RESULTS

Typical results for olefin pairs are shown in Figs 1–4 and Tables 1–3. In Fig 2 it should be noted that the reaction was carried out to appr. 90% *trans*-propenyl benzene disappearance. While the disappearance of *cis*-stilbene fits a first order plot well, a better agreement was generally ob-

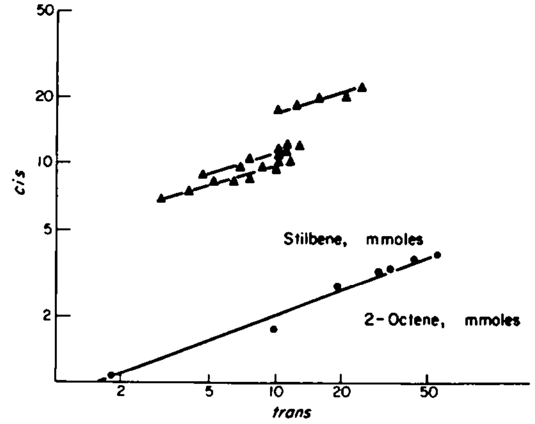


Fig 1. Relative rates of the *cis-trans*-stilbene pair, ▲, three different initial concentrations; and the *cis-trans*-2-octene pair, ●.

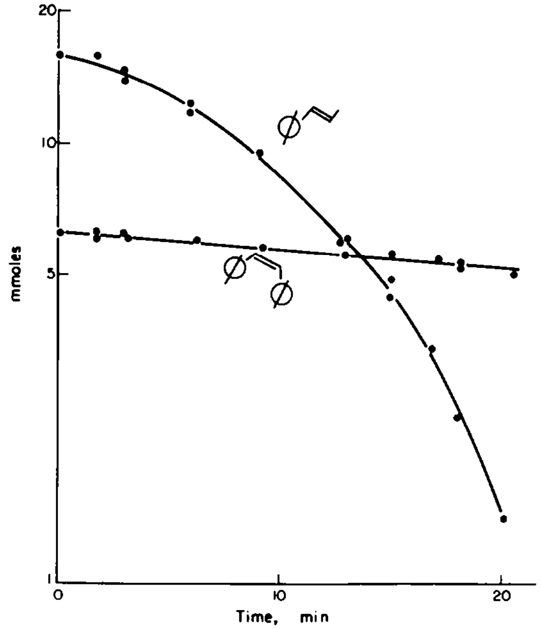


Fig 2. First order plot of the pair *trans*-propenyl benzene/*cis*-stilbene.

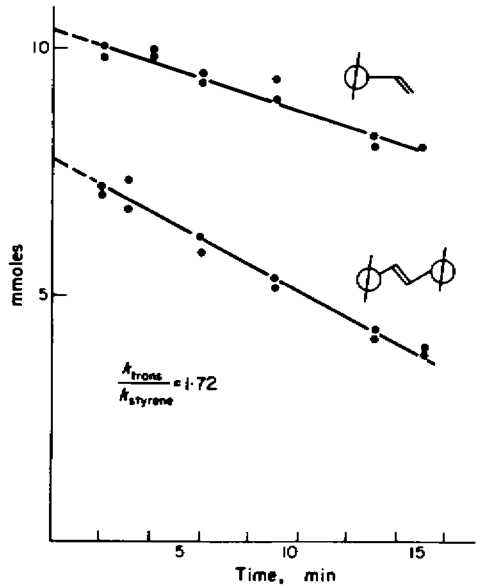


Fig 3. Zero order plot of the pair styrene/*trans*-stilbene.

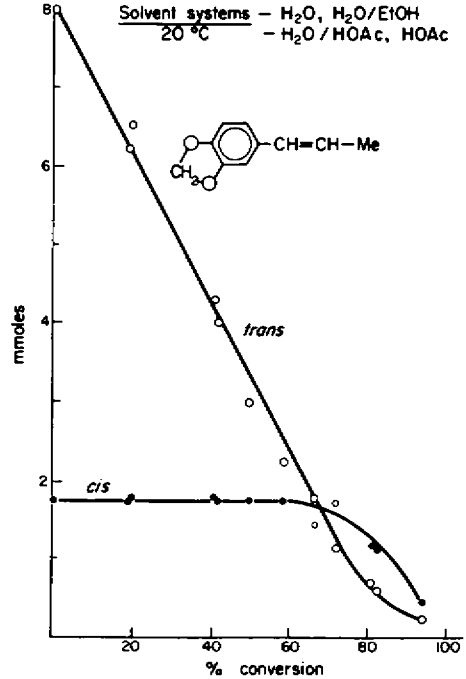


Fig 4. *cis-trans*-3,4-Methylendioxy propenyl benzene ozonizied in different solvent systems.

tained when all data for a particular run were fitted to a zero order plot (Figs 3 and 4). Curves were fitted by computer to zero and first order equations. Correlation coefficients (with one or two exceptions) were 0·91 or greater. In the example of Fig 2, a zero order plot gave a coefficient of 0·90, while a first order plot gave 0·91. A zero order plot for *trans*-propenyl benzene gave a value of 0·99. When conversions were low (< 40% of the faster-reacting olefin) correlation coefficients between zero and first order plots were very close. For example, zero order plots of *trans*-propenyl benzene and *trans*-stilbene showed values of 0·97 and 0·93, respectively; first order plots gave 0·99 and 0·945. But since the data gave a better fit to zero order kinetics when olefin conversions reached 60–90%, this treatment was used for comparison purposes. Typical relative rate data are shown in Tables 1 and 2. They are based on approximately a 1 : 1 concentration ratio of the two olefins used. In addition, a definite temperature effect (Table 3) on the rate ratio was observed with the higher temperature leading to a smaller rate difference, as expected.

Fig 4 is representative of the type of behavior observed when a large excess of one olefin is used. As another example, *trans*-stilbene can be ozonized exclusively in the presence of a small amount of *cis*-stilbene or styrene in carbon tetrachloride or methylene chloride. When the olefin concentrations become approximately equal, the relative rates become those shown in Table 2.

Table 1. Relative rates of olefin pairs at 0°

$$\frac{\textit{trans}\text{-Stilbene}}{\textit{cis}\text{-Stilbene}} = 2{\cdot}87$$

$$\frac{\textit{trans}\text{-Stilbene}}{\text{Styrene}} = 1{\cdot}72$$

$$\frac{\textit{trans}\text{-Stilbene}}{\text{Diethyl maleate}} = 74{\cdot}0$$

$$\frac{\text{Diethyl fumarate}}{\text{Diethyl maleate}} = 13{\cdot}0 \quad 11{\cdot}1\ (\text{calc})$$

$$\frac{\textit{trans}\text{-Stilbene}}{\textit{cis}\text{-Propenyl-benzene}} = 2{\cdot}31^{a}$$

$$\frac{\textit{trans}\text{-Stilbene}}{\text{1-Naphthyl-2-phenyl ethylene}} = 1{\cdot}00^{a}$$

[a] at 20°

Table 2. Relative rates
(based on Styrene = 1·00, at 0°)

p-MeO-*trans*-Propenylbenzene	> 5
trans-Propenylbenzene	3·00
trans-Stilbene	1·72
1-Octene	1·25
Styrene	1·00
cis-Propenylbenzene	0·67
cis-Stilbene	0·60
Diethyl Fumarate	0·26
Diethyl Maleate	0·023

Table 3. Effect of temperature on relative rate ratios *trans*/*cis*-ratio

	−20°	0°	20°
Stilbene	—	2·85 ± 0·25	2·42
Propenylbenzene	5·94 ± 0·35	4·46	—

Table 4. Rate constants for single olefins, k_{exp}
Solvent: CCl_4; 20 ± 0·5°C

Olefin	Concentration range (moles/l)	zero-order rate, M sec^{-1}
1-Octene	$1{\cdot}0 - 8{\cdot}38 \times 10^{-2}$	$8{\cdot}5 \pm 0{\cdot}3 \times 10^{-5}$
trans-Stilbene	$8{\cdot}32 \times 10^{-2}$	$8{\cdot}1 \pm 0{\cdot}3 \times 10^{-5}$
Styrene	$8{\cdot}55 \times 10^{-2}$	$7{\cdot}9 \pm 0{\cdot}3 \times 10^{-5}$
1-Naphthyl-2-phenyl ethylene	$3{\cdot}62 \times 10^{-2}$	$8{\cdot}3 \pm 0{\cdot}8 \times 10^{-5}$

In all cases of single olefins, the ozone–olefin reactions in carbon tetrachloride were found to follow zero order kinetics under the experimental conditions of constant ozone addition rate (Table 4). The rate constants for the zero order plots in Table 4 were determined from a least squares analysis of the data. This rate constant, k_{exp}, is defined by the following expression for a zero order rate;

$$\frac{-d[\text{olefin}]}{dt} = k[\text{ozone}]_0 = k_{exp}.$$

In carbon tetrachloride (or dichloromethane) there is neither a marked dependency on olefin structure or olefin concentration, and an experimental error of 10% in rate constant determination would account for most of the observed variation.

DISCUSSION

Possible explanations

(1) *Zero order kinetics.* In the stopped flow experiments of Cvetanovic,[1] the rate of olefin disappearance was expressed as:

$$\frac{-d[\text{olefin}]}{dt} = k[O_3][\text{Olefin}].$$

These kinetics apparently held only at very low olefin concentrations ($\sim 10^{-5}$ M), due to the limitations of the technique used and the rapidity of the ozonolysis reaction.

In present study, zero order kinetics were observed:

$$\frac{-d[\text{olefin}]}{dt} = k.$$

If the ozone and olefin were constant throughout the experiment, the above second order expression could explain the observed zero order kinetics. However, in the present experiments, the concentration of the olefin changed by at least 50% and one olefin (in the competition experiments) was sometimes depleted to 10% of its initial concentration, although at any given instant olefin could be present in large excess compared to the ozone concentration.

(2) The reaction is a heterogeneous physical process involving collisions between the gas bubbles and the olefin. This process was used by

Wagner and Greiner[7] to explain their experimental results. These authors used a range of gas flow rates; the lower range was 30 l/hr which is comparable to the range used here. Olefin conversion was reported to be a function of both gas flow rate and ozone concentrations but became independent of the former at sufficiently high flow rates. By the use of Schlieren optics it was concluded that the rate of reaction of ozone with the olefin was greater than the absorption rate into the solvent; it was estimated further that nearly each collision between olefin and ozone led to product. In our present study, this process would fail to explain the dependence of the relative rates of olefin loss (in the competition experiments) on olefin structure.

(3) The reaction may involve the formation of an intermediate reversible complex. The dependence of the rate on the olefin could be removed under certain experimental conditions.

Thus we may write

$$(1)\ A + O_3 \overset{k_1}{\rightleftharpoons} A^*$$

$$(2)\ B + O_3 \overset{k_2}{\rightleftharpoons} B^*$$

$$(3)\ A^* \xrightarrow{k_3} \text{product } P_A \xrightarrow{k_4} SP_A$$

$$(4)\ B^* \xrightarrow{k_5} \text{product } P_B \xrightarrow{k_6} SP_B.$$

where A and B are two different olefins, A* and B* are unspecified complexes (π- or σ-complexes) or reaction intermediates which can revert to reactants and P is the primary ozonide (3) which reacts to form stable products (SP).

$$\frac{d[P_A]}{dt} = \frac{-d[A]}{dt} = k_3[A^*]$$

$$\frac{d[P_B]}{dt} = \frac{-d[B]}{dt} = k_5[B^*].$$

The two cases of single olefin and olefin pairs are considered separately.

Case A: Single olefin

Since ozone is continuously introduced into the solution at a constant rate the amount of ozone actually present is very small relative to the olefin. Let A = olefin, A* = olefin–ozone complex, then the equilibrium constant K_1 is

$$K_1 = \frac{[A^*]}{([O_3]_0 - [A^*])[A]}$$

$$[A^*] = K_1[A][O_3]_0 - K_1[A][A^*]$$

$$= \frac{K_1[A][O_3]_0}{1 + K_1[A]}$$

$$\text{if } K_1[A] \gg 1 \quad [A^*] = [O_3]_0$$

i.e. in the limiting case all ozone introduced into the solution is immediately complexed by the olefin and, from (3)

$$\frac{-dA}{dt} = k_3[O_3]_0$$

i.e. zero order since ozone is constant.

Since k_3 and k_4 must be large, the question of a builtup of the complex does not arise. When $[O_3\text{-}A^*]$ is small relative to $[A^*]$ the condition of $K_1[A] \gg 1$ can be met. The close agreement between the rate constants, k_{exp}, for single olefins (Table 4) suggests that these values are independent of olefin structure. This finding itself then is no direct evidence for the participation of a complex in the reaction, at least not a complex where electronic or steric effects would affect K_1 under the conditions used. A builtup of 3, i.e. $k_3 > k_4$ apparently can only be observed under special conditions of temperature[6] or olefin structure.[11]

Case B: Two olefin competition

Ozonolysis of $8{\cdot}38 \times 10^{-2}$ m/l 1-octene gave a k_{exp} of $8{\cdot}5 \pm 0{\cdot}3 \times 10^{-5}$ M sec^{-1}, while $8{\cdot}32 \times 10^{-2}$ m/l *trans*-stilbene gave a value of $8{\cdot}1 \pm 0{\cdot}3 \times 10^{-5}$ M sec^{-1} for a ratio of rate constants of about one. When an equimolar mixture of these two olefins (total number of moles was $8{\cdot}88 \times 10^{-2}$ m/l) was ozonized the k_{exp} found were $5{\cdot}05 \times 10^{-5}$ M sec^{-1} (*trans*-stilbene) and $3{\cdot}68 \times 10^{-5}$ M sec^{-1} (1-octene), respectively, for a ratio of 1·37 (Table 2). Similar experiments gave the relative rate values summarized in Table 2; since most of the olefins contained at least one phenyl substituent, all rates were compared to styrene.

When two olefins are ozonized together their reactions no longer proceed independently. For an explanation of these observations Eq (5) is introduced.

$$A + B^* \rightleftharpoons A^* + B. \qquad (5)$$

Here A is a *trans*-isomer which has been shown to react faster and formation of the *trans*-isomer complex is therefore favored. K_1 and K_2 are modified as follows:

$$K_1 = \frac{[A^*]}{([O_3]_0 - [A^*] - [B^*])[A]}$$

$$K_2 = \frac{[B^*]}{([O_3]_0 - [A^*] - [B^*])[B]}.$$

Solving K_1 for A^*

$$[A^*] = K_1[O_3]_0[A] - K_1[A^*][A] - K_1[B^*][A]$$

$$[A^*] = \frac{K_1[A]([O_3]_0 - [B^*])}{1 + K_1[A]}$$

$$\text{if } K_1[A] \gg 1$$

then

$$[A^*] = [O_3]_0 - [B^*]$$

similarly

$$[B^*] = [O_3]_0 - [A^*]$$

then

$$\frac{-d[A]}{dt} = k_3[A^*]$$

$$\frac{-d[B]}{dt} = k_5[B^*].$$

From the definition of $K_e = [A^*][B][B^*]^{-1}[A]^{-1}$ and taking the rate ratio one obtains

$$\frac{-dA}{-dB} = \frac{k_3}{k_5} K_e \frac{[A]}{[B]}.$$

This expression is also consistent with the observersation that a large excess of A leads to almost exclusive ozonolysis of A. Since, under the conditions used here, 3 would not be observable, the ratio k_3/k_5 can be replaced by k_7/k_8 where these rate constants represent the overall rate of formation of SP_A from A^* and SP_B from B^*.

The nature of the complex is difficult to determine but it must be an intermediate on the path to the molozonide formed via 1,3-dipolar cycloaddition,[12] where eclipsing favors the *trans*-isomer, Fig 5; i.e. the *trans*-isomer would be expected to react faster. Cvetanovic[2] did not rule out a σ-complex provided it decomposed without geometric isomerization of the olefin. Intermediate 1 may be such a complex, although the particular olefin reported[5] could not undergo geometric isomerization. In view of the tentative evidence for a π-complex at low temperature[6] and in the case of 1-mesityl-1-phenyl ethylene,[13] a special structural situation, that form of olefin-ozone interaction cannot be ruled out. Further studies at very low temperature using the competition technique and spectral analysis are warranted. The relative rate data in Table 3 which show the effect of temperature in the expected direction, are in agreement with this suggestion.

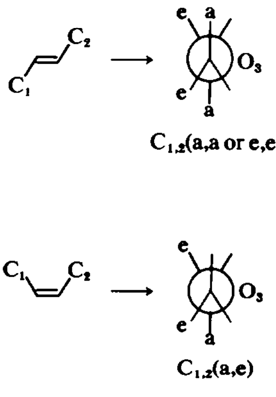


Fig 5. Newman projection of primary ozonide formation from *cis*- and *trans*-isomers.

An examination of the relative rate data in Table 2 leads to the conclusion that indirect steric effects have a more pronounced influence on the rate than electronic effects. This can be seen by a comparison of the stilbene and propenyl benzene data; the rate difference between the *trans-cis*-isomers is much greater than that between two different olefins of the same geometric configuration. The position of diethyl fumarate and diethyl maleate in the Table indicates that the overall trend in these reactions still is in agreement with the electrophilic tendency of ozone.

EXPERIMENTAL

Both single olefin and competition experiments were carried out as follows: Olefin solutions were prepared by diluting a weighed amount of olefin to either 100 or 1000 ml using either CCl_4 or CH_2Cl_2. Ozone was produced from oxygen at a constant rate by a Welsbach O_3-Generator (4 to 5×10^{-4} m/min); it was passed into the olefin solutions via a disperser and samples (0·2 ml–0·5 ml) were withdrawn at timed intervals and quenched with 0·1 ml of 0·1 N $Na_2S_2O_3$. Rates of ozone addition were such that no escape of ozone into a KI-trap was detected. Samples were analyzed in duplicate or triplicate by programmed temperature gas chromatography using a 5% SE 30 Silicone Gum Rubber Column. Diphenyl methane was used as an internal standard. Calculations showed that the expected stoichiometry of 1 mole of ozone added/1 mole of olefin consumed was nearly always correct. (O_3 generator settings: Pressure = 5·0 psi, Flow = 0·50 l/min, Voltage = 80–90 volts, resulting O_3 concentrations 36–44 mg/liter). Solvents used were carbon tetrachloride (Fisher certified and Fisher Spectranalyzed) and Methylene chloride (ACS-reagent grade).

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