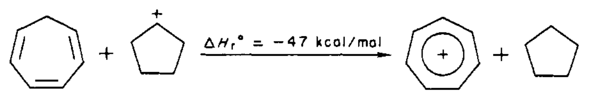
of charge delocalization over charge separation in the annulenones.



(15)

Conclusions

The published experimental value for $\Delta H_f^\circ(g)$ of diphenylcyclopropenone is too high by as much as 50 kcal/mol corresponding to a 2.5% error in the heat of combustion, possibly due to the presence of a small amount of impurity in the compound tested in the earlier work. More refined calorimetric measurements are in progress. The resonance stabilization in cyclopropenone appears to be in the range of 20 ± 5 kcal/mol. The value is about 6 kcal/mol greater than in methylenecyclopropene and lends support to the view that cyclopropenone has some ground-state aromatic stabilization.

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Kinetics of Ozonation. 1. Electron-Deficient Alkenes

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Abstract: Absolute rates of reaction of ozone with a series of alkenes bearing electron-withdrawing groups have been determined at several temperatures in CCl_4 by a stopped-flow technique. From these data, activation parameters have been calculated and range from those of tetrachloroethylene (E_a = 11 kcal/mol; log A(s^{-1}) = 6.0) to those of styrene (E_a = 3.1 kcal/mol; log A(s^{-1}) = 7.5) and 1-hexene (E_a = 2.4 kcal/mol; log A(s^{-1}) = 6.8). These results show that the ozonation of alkenes is quite sensitive to electronic effects, with electron-deficient alkenes reacting orders of magnitude slower than electron-rich alkenes. The rate of reaction of *trans*-1,2-dichloroethylene is about 25 times that of the cis or the 1,1 isomer, which is consistent with a 1,3-dipolar cycloaddition mechanism. Calculated entropies of activation also are consistent with this, but a general trend toward less negative entropies of activation with lower E_a suggests the possibility of a change in mechanism for more electron-rich alkenes.

Ozone is one of the most important toxins on a worldwide basis, responsible for lost work and illness to humans living in high-smog areas.[1-5] In order to model the reactivity patterns of ozone with the many potential targets in the lung, it is necessary to combine a knowledge of pulmonary physiology with the rate constants for the reactions of ozone with a wide range of biological molecules. Although the absolute rate constants for reaction of ozone with a large number of low molecular weight species have been measured in studies aimed at understanding the reactions that occur in gas-phase smog,[6-8] very few data are available for the reaction of typical organic and biological molecules with ozone in condensed phases. Therefore, we have begun a program to determine the absolute rate constants for reaction of ozone with major organic functional groups and with critical biological molecules and biopolymers.[9-12]

In this paper we report the rate constants for the halogenated olefins and other alkenes bearing electron-withdrawing groups. The rate constants at room temperature for the reactions of several of these compounds with ozone have been reported earlier, allowing a comparison of our data with literature values. However, few of the Arrhenius parameters have been previously reported, and we now provide those data.

Experimental Section

Purification of Carbon Tetrachloride. Carbon tetrachloride (Mallinckrodt, analytical reagent) was pretreated with a stream of ozone in oxygen for several hours at room temperature and then allowed to stand overnight. The solution was still blue after this time. After degassing under reduced pressure, no ozone or other peroxidic material reactive toward aqueous iodide remained in the carbon tetrachloride.

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Table I. Concentration Dependence of the Rate Constant of the Reaction of Ozone with *trans*-1,2-Dichloroethylene[a]

$[C_2H_2Cl_2]$, M	$10^3[O_3]$, M	k, L mol^{-1} s^{-1}
0.966	1	588
0.607	1	570
0.607	2	593
0.168	1	587
0.126	1	583
0.121	2	593
0.016	0.5	578
		av 585 ± 15

[a] All temperatures were 23.3 ± 0.5 °C.

Purification of Alkenes. All of the substrates in this study were of the highest purity commercially available. Additionally, tetrachloroethylene, trichloroethylene, and the dichloroethylenes were preozonated by passing a stream of ozone in oxygen over the rapidly stirred, neat alkenes at 0 °C and then distilled, collecting the middle third of the distillate. All other alkenes, with exception of vinyl bromide, were distilled prior to use. The alkenes used were as follows: tetrachloroethylene (Aldrich, 99+%), trichloroethylene (Aldrich, 98%), vinylidene chloride (Aldrich, 99%), *cis*-1,2-dichloroethylene (Aldrich, 97%), *trans*-1,2-dichloroethylene (Aldrich, 98%), 1,1-dichloro-1-propene (Pfaltz and Bauer), acrylonitrile (Kodak, 98%), vinyl bromide (Aldrich, 98%), methyl acrylate (MC/B), 1-chloro-2-methylpropene (Aldrich, 98%), allyl chloride (Kodak), allyl bromide (Aldrich), 1-hexene (Aldrich, 99%), and styrene (Aldrich, 99+%).

Alkene solutions were prepared from preozonated and freshly degassed CCl_4. Alternatively, the preozonized CCl_4 was stored over sodium carbonate and filtered prior to use. No significant differences were noted between these two techniques. Ozone solutions were prepared by bubbling a stream of ozone in oxygen through previously ozonated and degassed CCl_4 for ca. 1 h. These ozone solutions were about 3 mM[13] and were diluted to the desired concentrations with pretreated CCl_4.

Kinetic Measurements. Stopped-flow kinetics were carried out with a Hitech stopped-flow spectrophotometer (Model SF-3L) interfaced to an On-Line Instrument Systems Model 3820 data system.[14] The mixing chamber/flow-observation cell (2-mm light path) has a combined mixing/dead time of less than 6 ms. Experiments were conducted in a Freon 113 constant temperature bath in which the temperature was held constant to within ±0.5 °C. All reactions were followed at 290 nm, monitoring the disappearance of ozone. Unless otherwise stated, the ratio of alkene to ozone was at least 100.

A typical stopped-flow run consisted of collecting 100 points over 5 or more half-lives and a point representing at least five half-lives after this. The raw data from 3–5 runs were averaged to obtain a single measurement from which a pseudo-first-order rate constant was determined by exponential fitting.[15] Logarithmic plots of these data were linear throughout most of the course of the reaction with slopes similar to the values obtained via exponential fitting. From the pseudo-first-order rate constants, k', second order rate constants, k, were calculated as in eq 1.[16] Each reported second-order rate constant is an average of at least three such measurements.

$$k' = k[\text{alkene}] \qquad (1)$$

In some cases a series of measurements was carried out on a single prepared solution. However, for trichloroethylene, vinylidene chloride, *trans*-1,2-dichloroethylene, allyl bromide, allyl chloride, and 1-hexene, fresh solutions were prepared and duplicate or triplicate determinations consistently yielded results with no more than 10% variation. The results of several representative replications with *trans*-1,2-dichloroethylene are given in Table I.

Tetrachloroethylene, the least reactive of the compounds studied, was also investigated in a manner similar to that of Kurz and Pryor.[17] This involved adding C_2Cl_4 to a cuvette containing O_3 in CCl_4 and following the disappearance of ozone with time on a Varian Cary 219 spectrophotometer. Due to the slow rate of reaction of C_2Cl_4, its measurement is more susceptible to the effects of trace impurities, reaction of ozone with solvent, and gradual loss of ozone from the solution with time. Although we are less confident of our rate constant for the reaction of C_2Cl_4 with ozone compared to other values, our data indicate that the rate constant is significantly lower than that previously reported.[18]

Table II. Second-Order Rate Constants for the Reactions of Some Alkenes with Ozone in CCl_4[a]

	k, L mol^{-1} s^{-1}	
substrate	this work	lit.
C_2HCl_3	2.1	3.6,[b] 2.7[c]
cis-$C_2H_2Cl_2$	21.3	35.7[b]
1,1-$C_2H_2Cl_2$	25.4	22.1[b]
$CH_2{=}CHCN$	109[d]	100[e]
trans-$C_2H_2Cl_2$	590[f]	591[b]
allyl chloride	11 700	11 000,[b] 5 800[e]
1-hexene	110 000[h]	76 000,[g] 140 000[e]
styrene	135 000[i]	103 000,[b] 300 000[e] 109 000[j]

[a] Unless otherwise noted, all data were collected at 25 °C. [b] Reference 18. [c] Reference 25. [d] 17 °C. [e] Reference 20, 20 °C. [f] 24 °C. [g] Reference 19. [h] A 20-fold excess of substrate to alkene was used in these cases. [i] 20 °C. [j] Reference 26. This value was measured relative to *trans*-stilbene, for which the absolute rate was determined.

Results

The rate of reaction of ozone with *trans*-1,2-dichloroethylene was measured over a range of concentrations of both ozone and substrate, with little change in the calculated second-order rate constant. These data, collected in Table I, serve to illustrate that the process is first order in both reactants. This has also been shown by other authors.[18]

Some of the rate data determined from this work are collected in Table II, which also compares our values with the literature. Our values measured near room temperature are in general agreement with those of other authors, except for the rate of reaction of tetrachloroethylene. The only other differences are in the rates of the more reactive substrates, which is not surprising considering the difficulties in measuring very fast rates. Our values of k for both styrene and 1-hexene fall between those of Williamson and Cvetanovič[19] and those of Razumovskii and Zaikov.[20]

Second-order rate constants determined in this study at several temperatures are presented in Table III. For these data, the activation parameters E_a and log A have been calculated[16] and also appear in Table III.

Discussion

As reported by other authors,[18,20] the reactions of ozone with alkenes are very sensitive to electronic effects. The rate constants for the reaction with halogenated alkenes, or alkenes bearing other electron-withdrawing groups, are much lower than the rate constants for electron-rich alkenes. For example, vinyl bromide reacts about 100 times slower than 1-hexene, and acrylonitrile reacts slower still. The energies of activation also are consistent with this trend.

Our value of E_a for the reaction of 1-hexene with ozone in CCl_4 (2.4 kcal/mol) may be compared with the approximate value for the same substrate reported by Razumovskii in CH_2Cl_2 (0–2 kcal/mol),[21] of Wagner and Greiner for 1-dodecene in CCl_4 (<3 kcal/mol),[22] and the value of 2.5 kcal/mol for *trans*-2-butene estimated by Nangia and Benson.[23] Our value of E_a = 8.1 kcal/mol for the reaction of trichloroethylene with ozone in CCl_4 can be compared with the value of 9.0 kcal/mol in the same solvent.[24] The agreement between our results and the literature

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(13) We found some of our solutions to be about 3 mM in ozone by iodometric titration, so this approximate value was assumed throughout.

(14) On-Line Instrument Systems, Jefferson, GA.

(15) The analysis algorithm was written by Dr. K. Johnson (Pennsylvania State University, Department of Biochemistry, University Park, PA.) using a method of moments procedure. See: Dyson, R. D.; Isenberg, I. *Biochemistry* **1971**, *10*, 3233–3241.

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Table III. The Rates of Reaction of Alkenes with Ozone in CCl_4 at Various Temperatures[a]

alkene	T, K	k, L mol^{-1} s^{-1}	E_a, kcal mol^{-1} [b]	log A[c]
tetrachloroethylene	291.5	0.005[d]	11	6.0
	295.5	0.006[e] (0.002)		
	298.7	0.007[d]		
	307.2	0.010[e] (0.002)		
	317.4	0.024[e] (0.002)		
	331.1	0.041 (0.004)		
trichloroethylene	266.9	0.51 (0.04)	8.1	6.3
	296.2	1.84 (0.11)		
	298.1	2.06 (0.13)		
	307.3	3.38 (0.05)		
	317.3	5.39 (0.10)		
	325.5	7.94 (0.18)		
cis-1,2-dichloroethylene	274.7	7.5 (0.30)	7.0	6.5
	283.3	11.7 (0.15)		
	298.1	21.3 (0.32)		
	309.3	32.4 (0.12)		
	323.1	52.6 (0.40)		
1,1-dichloroethylene	267.3	7.77 (0.15)	6.2	6.0
	283.2	14.4 (0.70)		
	296.3	19.7 (0.60)		
	298.1	25.5 (1.1)		
	307.9	36.1 (1.2)		
	315.7	48.2 (1.4)		
1,1-dichloro-1-propene	253.5	30 (1.6)	6.0	6.6
	261.2	44 (1.2)		
	272.1	68 (1.1)		
	281.2	99 (2.4)		
	289.1	132 (3.5)		
	298.1	178 (3.2)		
acrylonitrile	254.3	26.8 (1.4)	5.8	6.4
	262.6	38.5 (2.6)		
	272.0	55.8 (1.1)		
	280.8	80.5 (1.4)		
	290.1	108.9 (3.2)		
	300.7	155.1 (5.6)		
trans-1,2-dichloroethylene	266.2	234 (3.2)	5.0	6.4
	283.2	400 (14)		
	287.7	452 (6)		
	296.2	620 (25)		
	296.7	590 (31)		
	307.4	830 (70)		
	310.3	825 (25)		
	313.7	960 (72)		
	318.7	1100 (78)		
vinyl bromide	258.1	242 (9)	4.9	6.7
	267.2	504 (18)		
	276.3	702 (16)		
	286.0	941 (21)		
	296.2	1245 (32)		
	303.9	1443 (18)		
methyl acrylate	255.8	1730 (170)	3.9	6.7
	265.1	2750 (240)		
	273.5	3220 (200)		
	285.2	4700 (175)		
	299.8	6400 (340)		
2-methyl-1-chloro-1-propene	267.7	4500 (400)	3.7	6.7
	274.2	5500 (350)		
	285.3	6560 (150)		
	295.3	8200 (700)		
allyl chloride	265.7	4800 (500)	3.4	6.5
	273.3	6800 (600)		
	296.7	9700 (260)		
	297.9	11700 (800)		
	307.4	12000 (550)		
	310.3	12100 (350)		
	313.7	14000 (1000)		
	318.7	14900 (350)		
allyl bromide	265.3	5900 (100)	3.3	6.6
	274.2	8600 (270)		
	285.3	11300 (430)		
	287.7	9600 (100)		
	295.3	13700 (300)		
	309.7	15100 (250)		
	318.7	19000 (600)		
	319.5	18200 (500)		

Table III (*Continued*)

alkene	T, K	k, L mol^{-1} s^{-1}	E_a, kcal mol^{-1} [b]	log A[c]
1-hexene[f]	266.5	50000 (3000)	2.4	6.8
	273.3	75000 (4000)		
	274.2	71000 (5000)		
	297.6	106000 (8500)		
	318.3	115000 (1800)		
styrene[f]	252.9	53300 (4500)	3.1	7.5
	262.5	75200 (8400)		
	273.1	109300 (11000)		
	282.6	120000 (15000)		
	293.3	135000 (16500)		
	302.8	152000 (19000)		

[a] k is the calculated second-order rate constant in L mol^{-1} s^{-1}. Parentheses give the error limits at 99% certainty. [b] The standard deviation of the slope of the plot of $1/T$ vs. log k multiplied by $2.303R$ was in all cases less than 0.1. [c] The standard deviation of the intercept of the plot of $1/T$ vs. log k was no greater than 0.05 in all cases. [d] These values were determined on a UV spectrophotometer by monitoring the absorbance of a solution of ozone and tetrachloroethylene in CCl_4 and plotting log $(A - A_\infty)$ vs. time. These data are not included in the calculation of E_a and log A. [e] The observed values of the pseudo-first-order rate constant was such that only a single significant figure could be obtained from the stopped-flow instrument in this case. [f] A 20-fold excess of substrate to ozone was used.

is reasonable since the earlier workers either used narrower temperature ranges than we did or a different solvent.

The energies of activation for the reactions of ozone with the other substrates studied are intermediate between those of 1-hexene and tetrachloroethylene. The dichloroethylenes have E_a of 7.0, 6.2, and 5.0 kcal/mol for the cis, 1,1, and trans isomers, respectively. Although a phenyl group is generally thought of as electron withdrawing, the rate constant for styrene at room temperature is higher than that of 1-hexene at the same temperature. However, the energy of activation is higher for styrene than for 1-hexene, and the greater reactivity of styrene is attributable to the entropy term.

The entropies of activation for all of the substrates in Table III, with the exception of styrene, may be described as -31 ± 2.5 eu. These values are consistent with the high degree of order expected for the transition state of a 1,3-dipolar cycloaddition, for which entropies of activation typically range from -29 to -40 eu.[25] Fliszár et al. have also noted very negative ΔS^* values for the ozonation of *cis*- and *trans*-stilbene and triphenylethylene.[26]

Also consistent with a highly ordered, cyclic transition state are the relative rates of reaction of *cis*- and *trans*-dichloroethylene. We, like Cvetanović,[19] observe that the trans isomer reacts at about 20 times the rate of the cis isomer. Fliszár et al. have noted a similar trend in the reactivity of cis- and *trans*-stilbene,[26] as has Razumovskii in the reactivities of fumaric and maleic acids in acetic acid.[27] Hoignê and Bader have noted the same trend in the ozonolysis of some alkenes in aqueous solutions.[28] This trend is generally followed for 1,3-dipolar cycloadditions since the substituents in a cis alkene are squeezed together in an eclipsed conformation in the transition state.[25] It is of interest to note that, according to our values, the difference in reactivity for *cis*- and *trans*-dichloroethylene is due almost entirely to the difference in E_a, not ΔS^*.

There is a slight trend toward less negative entropies of activation with increasing rates of reaction. This suggests that there is a slight lessening of the order of the transition state for more electron-rich substrates, which would be consistent with a change in mechanism.

Several authors have suggested that the attack of ozone on a double bond may proceed by two mechanisms, a 1,3-dipolar cycloaddition and a route with an intermediate and/or π complex.[9d,18,19,29-32] Bailey[33] and Mile et al.[34] have observed the reversible formation of an ozone–alkene π complex at low temperatures, which upon slight warming formed products.[9f] If Fliszár has presented some evidence that ozonations of electron-deficient alkenes are more likely to proceed via a single, electrophilic step, while electron-rich alkenes are most likely to react in a two-step process.[29] Such an argument is consistent with our findings. The entropy of activation would be expected to be more negative for a concerted pathway, and this is indeed what we observe for the more electron-deficient alkenes. This aspect of the reactivity of ozone toward alkenes will be explored further in a subsequent report when activation parameters are available for a wider variety of substrates.

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Registry No. Tetrachloroethylene, 127-18-4; trichloroethylene, 79-01-6; *cis*-1,2-dichloroethylene, 156-59-2; 1,1-dichloroethylene, 75-35-4; 1,1-dichloro-1-propene, 563-58-6; acrylonitrile, 107-13-1; *trans*-1,2-dichloroethylene, 156-60-5; vinyl bromide, 593-60-2; methyl acrylate, 96-33-3; 2-methyl-1-chloro-1-propene, 513-37-1; allyl chloride, 107-05-1; allyl bromide, 106-95-6; 1-hexene, 592-41-6; styrene, 100-42-5.

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