Appendix. Experimental Error Estimates in Linear Regression Analysis

All of the least-squares fits to straight lines in the Benesi–Hildebrand–Scott analyses (Tables I and II) and the evaluation of ΔH and ΔS (Table III) and of $\delta\Delta/\delta T$ (Table IV) were done using a weighted polynomial regression subroutine, LSE.[45] In the case of first-order polynomials (linear regression), this is identical with the method described by Worthing and Geffner.[46]

In this study, where four to eight points were fitted to a best straight line, we occasionally observed fortuitous coincidence of the points to the best line so derived. In such cases, the resulting extremely small standard deviations of intercept, δb_1, and of slope, δb_2, were not representative of the experiments which yielded the points.

We have, therefore, included in the standard deviations reported in this paper estimates of the error contributions arising from evaluable error ranges in the observed quantities, as follows. To each value y_i fitted to an equation such as (5) we assigned an error range δy_i.[47] Now the standard deviations δb_1 and δb_2 are both proportional to the square root of the sum of squares of residuals

$$\sum_i w_i r_i^2 = \sum_i w_i (y_i - b_1 - b_2 x_i)^2 \tag{19}$$

As a measure of the possible deviation of y_i from the line, we augmented the square of the residual, r_i^2, by the square of the error, $(\delta y_i)^2$. The calculation of standard deviations was then carried out in the usual way, with the sum of squares of residuals replaced by the quantity

$$\sum_i w_i [r_i^2 + (\delta y_i)^2]$$

To allow for skewed error distributions (for example, in the Benesi–Hildebrand–Scott analysis, the errors in the y_i's became larger at lower concentrations[47]), the points were assigned weights, w_i, inversely proportional to δy_i. All experimental quantities for which error estimates are given are reported as best value plus or minus the standard deviation computed by this method.

---

[45] LSE uses subroutines for which we are indebted to Dr. J. A. Plambeck and the University of Illinois Computing Center.

[46] A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943.

[47] In the case of the Benesi–Hildebrand–Scott analysis, where y_i is defined in eq 5, the error range of y_i is given by

$$(\delta y_i)^2 = (\delta d)^2/(\sigma - \sigma_A)^2 + [(\delta\sigma)^2 + (\delta\sigma_A)^2]d^2/(\sigma - \sigma_A)^4$$

where d is the donor concentration, δd is its estimated error (usually 0.005 *M*), and $\delta\sigma$ is the estimated error in shielding (usually 0.0017 ppm, *i.e.*, 0.1 Hz at 60 MHz).

Rates of Ozone–Olefin Reactions in Carbon Tetrachloride Solutions[1]

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

Contribution from the Division of Applied Chemistry, National Research Council of Canada, Ottawa, Canada.

Received January 22, 1968

Abstract: The values of the second-order rate constants (k_1) for the reactions of ozone with a number of simple alkenes have been determined at room temperature. The rates vary with olefin structure in a manner very similar to that found previously in this laboratory for the vapor-phase reactions of ozone with olefins. The results, therefore, confirm the vastly different behavior from the one observed in air-pollution studies at very low reactant concentrations. The reason for the difference is not clear.

Ozonation of olefins in solution at low temperatures has been the subject of many investigations.[3] Most of these studies have dealt primarily with product analysis and not with reaction rates. More kinetic work has been done with the aromatic compounds, which react with ozone considerably more slowly than do olefins. Nakagawa, Andrews, and Keefer[4] have determined ozonation rates of alkyl-substituted benzenes in carbon tetrachloride and acetic acid solutions and found excellent correlations of reaction rates with the number of alkyl substituents. The results show that ozone exhibits an electrophilic tendency in its attack on simple aromatic systems responding to the increased electron density in the aromatic ring at greater alkyl substitution.

Although no systematic determinations have been made of the rates of ozone attack on simple olefins in solution, a number of gas-phase investigations have been carried out. Ozone is a constituent of earth's atmosphere and also plays an important role in air-pollution phenomena. Most of the gas-phase work has been done from the point of view of ozone's implication in air pollution, and the concentrations of the reactants used have been intentionally kept very low (in the part per million range) to simulate the conditions in polluted atmosphere. In contrast to this, the gas-phase work from this laboratory[5,6] has been done at

---

[1] Issued as N.R.C. No. 10174.

[2] National Research Council Postdoctorate Fellow.

[3] P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

[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, 1063 (1960).

[6] Y. K. Wei and R. J. Cvetanovic, *ibid.* **41**, 913 (1963).

reactant concentrations some three orders of magnitude higher, *i.e.*, under conditions similar to those usually employed in standard gas kinetic studies. Unfortunately, there are serious discrepancies between the values of rate constants obtained in air-pollution studies by different workers and especially, for some olefins, between the low and the higher concentration work. Thus, in the higher concentration investigations in this laboratory, the internal olefins were found to react only slightly faster than the corresponding terminal olefins (including the 1,1-disubstituted ethylenes such as isobutylene), while in the air-pollution, low-concentration work they were found to react at least an order of magnitude more rapidly. Although such an exalted reactivity of internal olefins appears to be very unusual, a recent careful study by Bufalini and Altshuller[7] under the low-concentration conditions has confirmed the differences from the higher concentration values. For butene-2 the rates under the two sets of conditions differ by a factor as large as 10–15 and for trimethylethylene by an even larger factor of 20–40.

The large discrepancies in the gas-phase rate constant data for such potentially important reactions require further investigation of ozone–olefin reactions under a variety of conditions. As a first step in this direction, we have thought it necessary to determine *in solution*, using standard techniques, the rate constants for a number of representative ozone–olefin reactions. In the present paper we report the results of such determinations, including the relative (competitive) and also some absolute values of the rate constants.

Experimental Section

Relative ozonation rates were determined in Baker Adamson Reagent Grade carbon tetrachloride used without further treatment. Approximately 100 ml of carbon tetrachloride was ozonized by bubbling through it a 2% ozone–oxygen mixture from a Tower ozonizer apparatus for 60–90 min. After ozonation the resulting CCl_4 solution was pale blue, transparent, and smelled strongly of ozone. The solution showed strong absorption in the region of the ultraviolet where ozone absorbs in CCl_4.[4] The concentration of ozone after such treatment was determined iodometrically. A fresh ozone solution was prepared for each experiment. A thin-walled glass ampoule of approximately 4- or 5-ml volume was rinsed, then filled with the ozonized CCl_4, and placed into a 150 mm × 25 mm test tube containing about 4 ml of an olefin mixture in CCl_4 and either cyclohexane or *n*-pentane as marker compounds for the chromatographic analysis. All solutions volumes were measured with standard volumetric glassware. An interval of about 10–15 min was allowed for thermal equilibration since the thermal water bath temperature was 27.4 ± 0.2° while room temperature was 25 ± 1°. The ampoule was then quickly shattered, allowing the two solutions to mix rapidly. The total olefin concentration was always in excess of the ozone concentration. Olefin concentrations, relative to the marker, were measured before and after reaction with a Perkin-Elmer gas chromatograph equipped with a flame ionization detector. A 300-ft dinonyl phthalate capillary column was used for analysis. It was found that the ratio of peak heights of olefin to marker compounds was linear with olefin concentration.

In order to determine some absolute values of the rate constants in solution and to verify the relative rates determined by the competition experiments, a simple stopped flow apparatus was constructed. To mix the solutions rapidly and establish a steady-state condition in the quartz reaction vessel, the solutions were driven from each of two bottles at equal rates by N_2 at 15–20 psig pressure into a 4-mm spring-loaded three-way stopcock which served as a mixing chamber. The total flow rate was 80–100 cm^3/sec. From the tap, the reactant solution passed through 3 cm of 4-mm i.d. tubing, 5 cm of 3-mm i.d. tubing, and then into the reaction cell very near to the front window. The 100-mm path-length cell (volume $\simeq 11$ cm^3) was firmly mounted in the 100-mm cell compartment of a Beckman Model DU spectrophotometer equipped with an energy recording adapter. The output voltage was measured with a Hewlett-Packard 7100B recorder with a 0.5-sec full-scale response time. Only about 25% of the recorder scale was used in the experiments. The circuit time constant appeared to be limited by the recorder response time.

For determining the absolute rates it was necessary to pretreat the carbon tetrachloride to prevent the decomposition of ozone (about 30%/hr) caused by impurities in the CCl_4. The following pretreatment is similar to that used in ref 4. Ozonized oxygen was bubbled through the CCl_4 for approximately 1 hr, and the ozone was then displaced from solution with dry N_2. The emergent N_2 gas was tested for O_3 by bubbling it through an aqueous KI solution. When no ozone was detected in this way, the solvent was presumed to be free from ozone. If the ozone had not been completely removed, the solvent showed an increase in transmittance after the olefin was added to it. This provided another test for residual O_3 in the carbon tetrachloride.

Phillips research grade olefins, with the exception of Aldrich research grade tetramethylethylene, were used in all experiments. Eastman reagent grade cyclohexane and Phillips research grade pentane were used as marker compounds.

Results

With the low olefin and ozone concentrations in the present experiments, no volatile products detectable with gas chromatography as described above were generated at room temperature. Apparently, a large fraction of the reaction products under these conditions are of low volatility and hence were not observed chromatographically on the columns used. No attempt was made to use other techniques in order to isolate and characterize the products, and the primary emphasis was placed on a determination of reaction rates and the stoichiometry of the reaction.

The stoichiometry of the ozone–1-hexene reaction was determined from the amount of 1-hexene consumed in a reaction with a known quantity of ozone dissolved in carbon tetrachloride. A measured volume of ozone solution of known concentration was placed in a thin-walled ampoule which was then broken while submerged in a known amount of 1-hexene solution at room temperature. Another similar ampoule was broken under KI solution, and the ozone concentration was determined iodometrically. This procedure was expected to minimize the error due to ozone escaping from solution. The results of determinations at two different ratios of initial reactant concentrations are given in Table I. The small discrepancy between 1 : 1 stoichiometry and the measured values is probably not significant and may be due to ozone escaping from the CCl_4 solution of olefin more effectively than from the KI solution. It is also conceivable that ozone reacted with small amounts of oxidizable impurities present in the CCl_4 to form compounds capable of oxidizing I^- to I_2.

Table I. Stoichiometry of the 1-Hexene–Ozone Reaction

Initial reactant concn, *M*		(1-Hexene)$_0$/(O_3)$_0$	Δ moles of 1-hexene/Δ moles of O_3
O_3	1-Hexene		
2.80×10^{-3}	1.00×10^{-2}	3.57	0.96
3.38×10^{-3}	0.50×10^{-2}	1.48	0.95

---

(7) J. J. Bufalini and A. P. Altshuller, *Can. J. Chem.*, 43, 2243 (1965).

Relative reaction rates of ozone with different olefins were determined by the competitive technique. If two olefins compete with each other for ozone, then eq 3, derived below, relates the ratio of rate constants to their respective change in concentration in the course of the reaction.

$$O_3 + \text{olefin}_1 \xrightarrow{k_1} \text{products} \tag{1}$$

$$O_3 + \text{olefin}_2 \xrightarrow{k_2} \text{products} \tag{2}$$

$$\frac{d(\text{olefin}_1)}{d(\text{olefin}_2)} = \frac{k_1(\text{olefin}_1)}{k_2(\text{olefin}_2)} \tag{3}$$

Upon integrating (3)

$$\frac{k_1}{k_2} = \frac{\log\left[\dfrac{(\text{olefin}_1)_{\text{final}}}{(\text{olefin}_1)_{\text{initial}}}\right]}{\log\left[\dfrac{(\text{olefin}_2)_{\text{final}}}{(\text{olefin}_2)_{\text{initial}}}\right]} \tag{4}$$

Equation 4 was derived assuming that no other processes occur which remove significant amounts of olefin. Ozone can be removed by other processes but still have no effect on the relative rates calculated from eq 4. If olefins were being removed by processes other than reaction with O_3, the expected ratio of (olefin used/ozone added) would be greater than 1. That this is not the case is indicated by the results in Tables I and II. In most cases the ratio (olefin used/ozone added) is near unity or somewhat less than unity.

Attempts were made to determine the relative rates of C_2H_4 and C_3H_6 by the same method. However, approximately 70% of the C_2H_4 dissolved in CCl_4 at about 5×10^{-3} *M* escaped from solution while the procedure was carried out. Similarly about 20% of the propylene was lost. The butenes showed only a small loss, for which allowance was made by preparing a blank treated in the same way as the reactant solution except that an ampoule containing only pure CCl_4 without O_3 was broken in the butene solution.

The experimental errors in the relative rate constants summarized in Table II are about ±10%, as determined by cross checking the relative rates for *cis*-2-butene, trimethylethylene, and tetramethylethylene.

Absolute values of the rate constants k_1 for reaction 1 were determined with 1-hexene, 2-hexene, and 1-pentene. Since reaction 1 is quite rapid, and because of the limitations of the simple stopped-flow system, it was necessary to work in the region where the reaction was first order in both ozone and olefins. Initial reactant concentrations were normally $0.5\text{–}2.0 \times 10^{-5}$ *M*. Second-order dependence held over 90% of the reaction range. The data were plotted according to eq 5,

$$\frac{2.3}{(\text{Ol})_0 - (O_3)_0} \log \frac{(O_3)_0(\text{Ol})}{(\text{Ol})_0(O_3)} = k_1 t \tag{5}$$

where $(\text{Ol})_0$ = initial olefin concentration, $(O_3)_0$ = initial ozone concentration, (Ol) = olefin concentration at time *t*, and (O_3) = ozone concentration at time *t*. Figures 1, 2, and 3 show second-order plots for 1-hexene, 2-hexene, and 1-pentene, respectively. The results are summarized in Table III (column 2). The value obtained for hexene-1 has been used to convert the relative rate constants from Table II to the absolute values listed in column 3 of Table III.

Table II. Summary of Competitive Experiments. Relative Rates of Ozonation of Olefins at 27.4 ± 0.2°[a]

Olefin A	Olefin B	Moles of olefin consumed/moles of O_3 added	k_B/k_A
Cyclopentene (B) *vs.* 1-Hexene (A)			
5.0×10^{-3}	8.9×10^{-3}		2.49 ± 0.04
5.0	2.5	1.0 ± 0.2	2.42 ± 0.3
5.0	5.0		2.51 ± 0.2
		Mean	2.47 ± 0.2
Trimethylethylene (B) *vs.* 1-Hexene (A)			
5.0×10^{-3}	5.0×10^{-3}	1.02 ± 0.07	2.16 ± 0.08
5.0	3.0	1.07 ± 0.04	2.23 ± 0.1
3.0	5.0	1.05 ± 0.06	2.18 ± 0.19
		Mean	2.19 ± 0.1
Tetramethylethylene (B) *vs.* Cyclopentene (A)			
5.0×10^{-3}	5.0×10^{-3}	1.11 ± 0.07	0.916 ± 0.012
3.0	5.0	1.01 ± 0.05	0.934 ± 0.02
5.0	3.0	0.84 ± 0.02	0.948 ± 0.004
		Mean	0.931 ± 0.01
Trimethylethylene (B) *vs.* Cyclopentene (A)			
4.0×10^{-3}	4.0×10^{-3}	1.19 ± 0.1	0.94 ± 0.01
Tetramethylethylene (B) *vs.* 1-Hexene (A)			
5.0×10^{-3}	5.0×10^{-3}	0.90 ± 0.05	2.63 ± 0.3
1-Pentene (B) *vs.* 1-Hexene (A)			
5.0×10^{-3}	5.0×10^{-3}	0.58[b]	1.05 ± 0.04
5.0	5.0	0.69[b]	1.08 ± 0.06
3.0	5.0	0.88	1.06 ± 0.01
		Mean	1.06 ± 0.04
1-Pentene (A) *vs.* Isobutylene (B)			
5.0×10^{-3}	5.0×10^{-3}	0.81	1.23 ± 0.02
3.0	5.0	0.81	1.22 ± 0.01
5.0	3.13	0.98 ± 0.04	1.17 ± 0.02
		Mean	1.21 ± 0.02
1-Hexene (A) *vs.* 2-Hexene (B)			
5.0×10^{-3}	5.0×10^{-3}	0.81	2.13 ± 0.22
4.0	4.0	0.94	1.90 ± 0.07
2.5	2.5	0.78	1.78 ± 0.07
		Mean	1.94 ± 0.12
1-Pentene (A) *vs.* *cis*-2-Butene (B)			
5.0×10^{-3}	3.05×10^{-3}	0.86	2.35 ± 0.1
3.0	3.0	0.76	2.36 ± 0.02
3.0	4.5	0.85	1.94 ± 0.16
		Mean	2.22 ± 0.09
2-Hexene (A) *vs.* *cis*-2-Butene (B)			
5.0×10^{-3}	4.5×10^{-3}	0.87	0.98 ± 0.02

[a] Concentration in moles/l. [b] These low values were found to be due to excessive consumption of ozone by the impurities in the particular batch of CCl_4 used in these two experiments.

Discussion

The primary objective of the present work has been to determine the rates of ozone attack in solution on several representative olefins. This information is necessary in order to establish whether the rates with internal olefins are indeed very much faster than with terminal olefins, as indicated in the air-pollution studies, for example, by Bufalini and Altshuller,[7] at very low reactant concentrations (*ca.* 4×10^{-8} *M*). The relative rates obtained by several workers are compared in Table IV. It is evident that the trend observed in the present work in carbon tetrachloride solutions at reactant concentrations of *ca.* 2×10^{-3} *M* is very similar

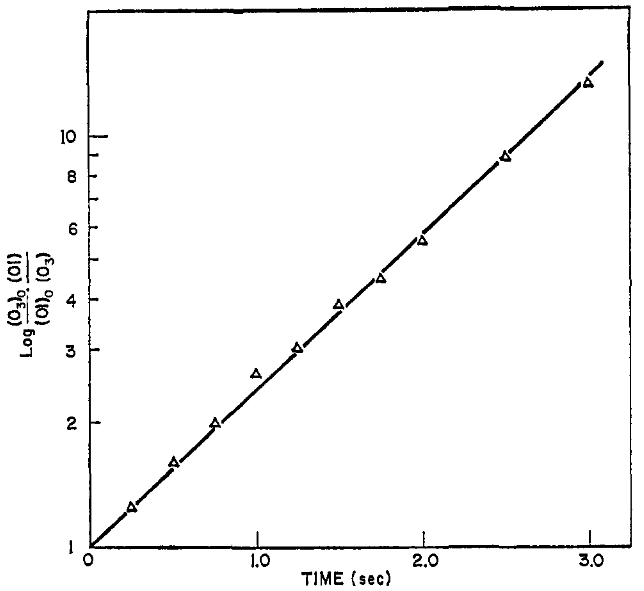

Figure 1. Determination of the absolute rates of ozonation. Plot of eq 5 for 1-hexene.

to that found previously in this laboratory in the gas phase at relatively high concentrations of *ca.* 10^{-4} to 10^{-5} *M* by Vrbaski and Cvetanović[5] and by Wei and Cvetanović.[6] Slight differences between these values are very minor when compared to the differences from the results of Bufalini and Altshuller. The reason for a large discrepancy between the relative rates under the air-pollution conditions, *i.e.*, at very low reactant concentrations in the gas phase, and those at much higher concentrations in solution and in the gas phase is not clear. Experimental errors of such magnitudes must be ruled out. An obvious difference is in the reactant concentrations, and a systematic study of the dependence of the rates on a variation of reactant concentrations over several orders of magnitude would seem to be necessary before the discrepancy could be resolved.

Table III. Absolute Rate Constants (k_1) for Olefin Ozonation Reactions

Olefin	Abs detn, M^{-1} sec^{-1} (25 ± 1°)	Based on rel values in Table II,[a] M^{-1} sec^{-1} × 10^{-5} (27.4°)
1-Hexene	$0.76 \pm 0.12 \times 10^5$	0.76
1-Pentene	$0.76 \pm 0.1 \times 10^5$	0.81
2-Hexene	$1.7 \pm 0.3 \times 10^5$	1.48
Isobutylene		0.97
cis-2-Butene		1.63
Trimethylethylene		1.67
Tetramethylethylene		2.00
Cyclopentene		2.00

[a] Calculated from the relative values (Table II) taking for hexene-1 the absolute value $k_1 = 0.76 \times 10^5$ l. mole^{-1} sec^{-1} determined in the present work.

The trend in the ozonation rates with the molecular structure of the olefins observed in the present work is very similar to that observed previously in this laboratory in the gas phase and discussed at some length in the earlier publications.[5,6] The present solution data do not appear to reveal any significant new features and in particular show once again the very small effect of alkyl substituents in simple alkenes on the rates of ozone attack. More pronounced substituent effects have now been observed in a parallel study of the ozone reactions with chlorinated ethylenes.[8] The mechanistic implications of the trends in the rates with olefin structure will be discussed in conjunction with the results obtained with chlorinated ethylenes[8] and will not be repeated here.

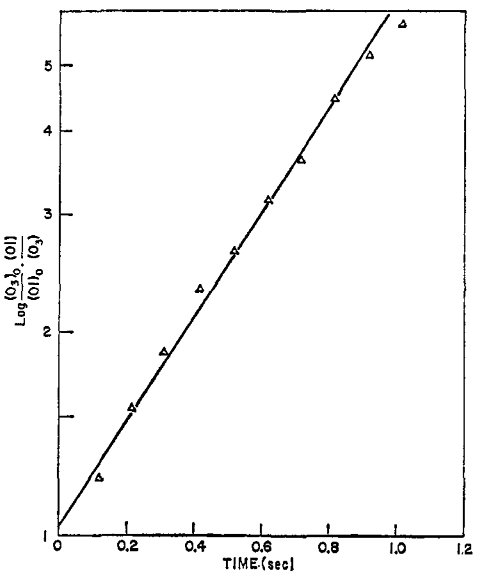

Figure 2. Determination of the absolute rates of ozonation. Plot of eq 5 for 2-hexene.

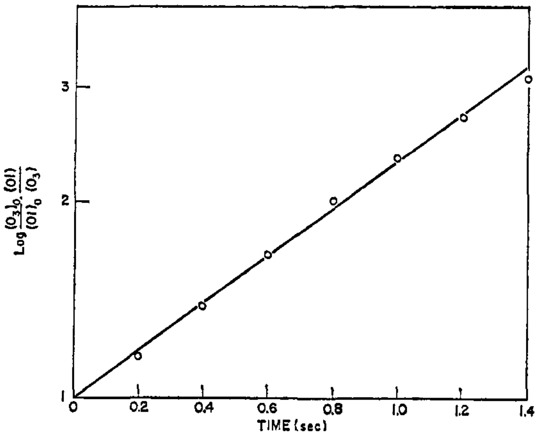

Figure 3. Determination of the absolute rates of ozonation. Plot of eq 5 for 1-pentene.

Mutual consistency of the rates obtained in the present work has been checked by cross-determination of relative rates (Table II) and also by comparing the absolute rates for 1-hexene, 1-pentene, and 2-hexene with the corresponding relative values obtained by the competitive technique. The values obtained by the two techniques are, within the likely experimental errors, the same, as shown by entries in columns 2 and 3 of Table III.

The absolute values of the rates of ozone attack on olefins in carbon tetrachloride solution determined in the present work are appreciably larger than the values

---

(8) D. G. Williamson and R. J. Cvetanović, submitted for publication.

Table IV. Comparison of Relative Rates of Ozonation of Olefins

Olefin	Vrbaski and Cvetanović[a]	Wei and Cvetanović[b] O_2	N_2	Bufalini and Altshuller[c]	This work
1-Hexene	1.0	1.0	1.0	1.0	1.0
1-Pentene	0.8	0.9	0.8	...	1.1
Isobutylene	0.8	0.8	1.0	2.0	1.3
cis-2-Butene	2.9	2.7	1.4	29	2.1
2-Hexene	2.7	2.9	2.5	...	1.9
Trimethylethylene	2.5	2.8	3.0	65	2.2
Tetramethylethylene	3.0	3.8	5.2	...	2.6
Cyclopentene	...	...	...	...	2.6

[a] Reference 5. [b] Reference 6. The two columns refer, respectively, to values obtained with O_2 and N_2 as the diluent gas. [c] Reference 7.

of the corresponding rates in the gas phase. This can be seen, for example, by comparing the rates of ozonation of hexene-1 in the two media. For this reaction the gas-phase values of k_1 obtained by different workers agree quite well.[7] The present value of k_1 for hexene-1 in CCl_4 solution is 13 ± 4 times greater than the gas-phase values for the same reaction. Such a large ratio ($R_{s/g}$) of the rate constants k(solution)/k(gas) need not be regarded as unexpected since order-of-magnitude calculations[9,10] predict for second-order reactions $R_{s/g}$ values as large as one to two powers of ten. However, it would seem at the moment that few experimental data can be quoted in support of these predictions and, in some cases, there is little or no difference between the rates in the gas phase and in solution. Relative rates of a series of reactions of the same type should be affected little on going from the gas phase to solution. This seems to be borne out by the present results and the gas-phase results obtained previously in this laboratory.

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism,' 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 7.

(10) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 504–510.

Reactions of Titanium Tetrachloride with BCl_3, $(CH_3)_2NBCl_2$, $[(CH_3)_2N]_2BCl$, $[(CH_3)_2N]_3B$, $[(CH_3)_2N]_2BCH_3$, and $B_2[N(CH_3)_2]_4$[1a]

G. S. Kyker[1b] and E. P. Schram[1c]

Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210. Received November 2, 1967

Abstract: Treatment of titanium tetrachloride with bis(dimethylamino)chloroborane, $[(CH_3)_2N]_2BCl$, or tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, results in the formation of di[bis(dimethylamino)chloroborane]tris[tetrachlorotitanium(IV)], $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$. Reaction with bis(dimethylamino)methylborane, $[(CH_3)_2N]_2BCH_3$, affords dimethylaminochloromethylborane, $(CH_3)_2NBClCH_3$, and dimethylaminotrichlorotitanium(IV), $(CH_3)_2NTiCl_3$; with tris(dimethylamino)borane, $B[N(CH_3)_2]_3$, the products of reaction are $[(CH_3)_2N]_2BCl$, dimethylaminodichloroborane, $(CH_3)_2NBCl_2$, bis(dimethylamino)dichlorotitanium(IV), $[(CH_3)_2N]_2TiCl_2$, and $(CH_3)_2NTiCl_3$. Boron trichloride was found to be unreactive as would be expected, while dimerization of $(CH_3)_2NBCl_2$ took place in the presence of excess $TiCl_4$.

The reaction of titanium tetrachloride with tetrakis(dimethylamino)diborane(4), $B_2[N(CH_3)_2]_4$, was investigated as a possible route to the synthesis of compounds containing Ti–Ti covalent bonds. Rather than formation of species containing metal–metal bonds, bis(dimethylamino)chloroborane was produced and subsequently complexes with $TiCl_4$ to afford $\{[(CH_3)_2N]_2BCl\}_2\{TiCl_4\}_3$. In order to elucidate the factors associated with this stoichiometry, reactions of $TiCl_4$ with $[(CH_3)_2N]_2BCl$, $[(CH_3)_2N]_2BCH_3$, $[(CH_3)_2N]_3B$, $(CH_3)_2NBCl_2$, and BCl_3 were investigated.

Experimental Section

Apparatus. All reactions were carried out in a section of a standard vacuum line isolated from mercury and equipped with stopcocks lubricated with a Kel-F 200 wax–Fluorolube blend which was found to be inert to gaseous and liquid titanium tetrachloride. Manipulations of nonvolatile materials were effected in a dry nitrogen atmosphere inside a glove box. General Dynamics "Hi-Pure" nitrogen was dried by passage through a tube containing Linde Molecular Sieve 4A, and the absence of residual moisture was assured by employing a P_2O_5 dessicant. Vapor-tension measurements were performed with a triple Pyrex spoon gauge (P_{obsd} ±0.2 torr in the range 1.0–80.0 torr). Melting points of volatile materials were determined, *in vacuo*, using the falling rod method.[2] Analyses for titanium, boron, chlorine, and nitrogen were by ignition to TiO_2

---

(1) (a) G. S. Kyker and E. P. Schram, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. O-063; (b) work carried out in partial fulfillment of the M.S. degree; (c) to whom correspondence should be addressed.

(2) A. Stock, *Ber.*, 50, 156 (1917).