A Method for Measuring the Activation Volumes of Fast Reversible Reactions. The Ferric Thiocyanate Complex

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Abstract: By using commercially available high-pressure optical cells and auxiliary equipment it is possible to produce pressure jumps within any two limits in the kilobar range. With an optical path of 2 cm the mechanical relaxation time can easily be reduced to 6 msec. Chemical relaxation can be observed by optical analysis and used to find reaction rates at any pressure within the working capacity of the apparatus. The method has been applied to the reaction of ferric ion with thiocyanate ion, and its activation volume is 5–6 ml/mol. The total volume change was evaluated by measuring the effect of pressure on optical density and found to be 17.5 ml.

In recent years the measurement and interpretation of activation volumes has become a useful tool in the study of reaction mechanisms.[1] Up to the present, however, the technical difficulty of quickly initiating and sampling reaction mixtures under high pressure has limited the application of the method to reactions having half-lives of not much less than 1 hr. In order to circumvent this limitation and undertake the study of the generally fast substitution reactions of inorganic complexes, we set out to develop a pressure-jump perturbation method which could be used at any pressure up to 1 or 2 kbars.

Pressure jumps from 30 to 50 atm down to 1 atm have already been applied to the kinetics of fast reactions[2,3] including the formation of the ferric thiocyanate complex[2c] which is the object of the present study. In previous work the pressure has usually been applied by gas from a commercial storage cylinder and released by rupture of a diaphragm. This technique gives very quick pressure jumps of less than 1-msec duration, but the perturbations have been small and difficult to measure accurately. Suppose, for example, that the process in question is the interconversion of two substances, A and B, which differ in molar volume by an amount, ΔV. The magnitude of the perturbation can be calculated from (1). For the most favorable case,

$$d \ln K/dP = \Delta V/RT = \Delta \ln (C_B/C_A)/\Delta P \qquad (1)$$

assume the measured property is directly proportional to C_B, and $C_B \ll C_A$. If $\Delta P = 50$ atm and $\Delta V = 20$ ml, the relative change in property is 4%. By producing the pressure jumps in apparatus specially constructed to withstand high pressures, we had hopes of creating larger perturbations even in processes having smaller ΔV, and, what is more important, to determine simultaneously the effect of pressure on reaction rate.

Experimental Section

Apparatus. A schematic diagram of the apparatus is given in Figure 1. The high-pressure pump, gauge, valves, tubing, and fittings were obtained from a variety of commercial sources. The optical cell was obtained from the Superpressure Division of the American Instrument Co., Catalog No. 11-550. It has quartz windows with a clear aperture of 1 cm and a path length of 1 cm. The sample was isolated from the pressurizing fluid by a deformable cell shown in Figure 2.

Operating Procedure. With both cutoff valves open the desired final pressure was generated in the reservoir. The range of final pressures was from 50 to 1360 atm. The reservoir was then isolated, and the desired initial pressure was generated in the optical cell. In most cases the initial pressure was either 250 atm higher or lower than the final pressure. Both cutoff valves were closed for 1 min in order to dissipate the thermal effects of compression or expansion, and the valve between the optical cell and reservoir was then opened. The output of the photomultiplier was bucked by an adjustable external emf so that even a small change in optical density could be made to cause a full-scale deflection of the oscilloscope. A camera recorded several sweeps of the oscilloscope with the sweep period adjusted to approximately half the relaxation time (usually 100–300 msec).

Correction for Heat of Adiabatic Expansion or Compression. A thermocouple was placed in the sample space of the optical cell and it was filled with water. The temperature jump was accurately proportional to the pressure jump up to 1360 atm with a coefficient of 1.07×10^{-3} deg/atm. The increase in heat content is approximately equal to $P\Delta V$, where P is the upper pressure. By using the recorded activation energy for the formation of ferric thiocyanate complex,[4] we calculated a correction factor of 6% for relaxation times following pressure jumps of 250 atm.

Reaction Solutions. Solutions containing ferric perchlorate, potassium thiocyanate, and perchloric acid were prepared in such concentrations as to duplicate the results of Below, Connick, and Coppel,[4] who made a very careful study of the kinetics by a variation of the stopped-flow method.

The Effect of Pressure on the Equilibrium Constant. In order to determine the effect of pressure on the dimensions of the sample cell, a basic solution of methyl orange indicator was placed in it. There was no change in the photomultiplier anode current when the pressure was increased to 1360 atm. Evidently the compression of the dye (~5% increase in concentration) and the distortion of the cell compensated fortuitously. The cell was then filled with a portion of a mixture of 0.788 ml of 0.100 *M* KSCN, 4.576 ml of 0.0200 *M* $Fe(ClO_4)_3$, and 10 ml of 1.00 *M* $HClO_4$ which had been diluted to 50 ml. According to the best determination of the equilibrium constant[4] this solution contained the following species at 25°: 0.000576 *M* $FeSCN^{2+}$, 0.00400 *M* Fe^{3+}, 0.00100 *M* SCN^-. The absorbance, A, was measured at various pressures up to 1360 atm, using a filter with maximum transmission at 515 mμ and a half-band-width of 30 mμ, and the concentration of $FeSCN^{2+}$ was assumed to be proportional to A. The values of ($FeSCN^{2+}$) thus obtained were used to calculate values of K (Table I). Figure 3 is a graph of $\Delta \ln K$ *vs.* P which is nearly a straight line as implied by eq 1. The slope gives a value of +17.5 ml for ΔV.

Direct Determination of ΔV. In order to obtain a measurable change of volume, it was necessary to use much higher concentra-

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[1] W. J. le Noble, *J. Chem. Educ.*, **44**, 729 (1967).

[2] (a) H. Strehlow and M. Becker, *Z. Elektrochem.*, **63**, 457 (1959); (b) H. Wendt and H. Strehlow, *ibid.*, **64**, 131, 1107 (1960); (c) H. Wendt and H. Strehlow, *ibid.*, **66**, 228 (1962).

[3] P. A. Hurwitz and G. Atkinson, *J. Phys. Chem.*, 71, 4142 (1967).

[4] J. F. Below, Jr., R. E. Connick, and C. P. Coppel, *J. Amer. Chem. Soc.*, 80, 2961 (1958).

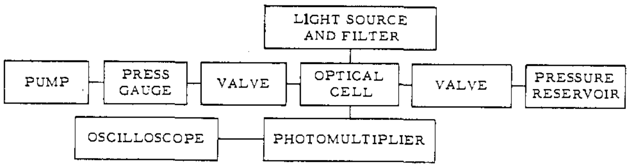

Figure 1. Pressure-jump apparatus.

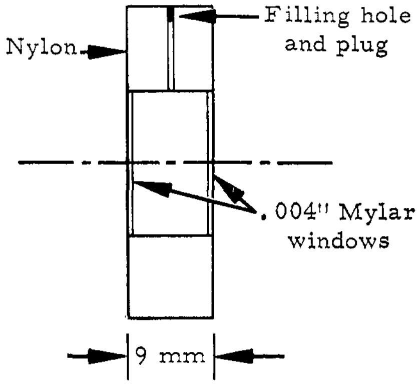

Figure 2. Deformable sample cell.

tions of reactants than those used in the kinetic study, and to attempt a correction for the effects of dilution. The reaction was carried out in a dilatometer having the same form as the Ostwald viscosimeter. The bulb has a capacity of 14.5 ml and the capillary arms contain 1.06 μl/mm. A 5-ml portion of 0.8 *M* KSCN was placed in the bulb, and beneath it was placed 9.5 ml of 0.5 *M* $Fe(NO_3)_3$ which was 1 *M* in HNO_3. A thin dark layer of complex ion separated the two solutions. After thermal equilibration, the liquid levels in the capillary arms were measured, and the solutions were mixed by inverting the apparatus several times. After reequilibration of the temperature, the liquid levels were measured again, and the change of volume was calculated. By assuming $K = 144\ M^{-1}$ it was calculated that the final concentration of $FeSCN^{2+}$ was 0.246 *M* and that of free SCN was 0.020 *M*. The value of ΔV at this concentration is +8 ml.

Table I

P (atm)	1	340	540	810	1080	1360
K (M^{-1})	(144)	118	101	84	70	54

In order to correct ΔV for the effects of dilution we used the data given by Gucker[5] for the coefficient of apparent molar volume with respect to the square root of concentration for a number of electrolytes. The coefficient for the 3:1 charge type is not given, but there are theoretical grounds for believing it should be the geometric mean of the coefficients of the 2:1 and 4:2 types which were given. A value of 15 ml/mol $M^{1/2}$ was adopted. The values for the 1:1 and 2:1 electrolytes are 2, and 5, respectively. By means of these coefficients it was calculated that the value of ΔV at high dilution would be +17 ml.

Measurements of Mechanical Relaxation Time. The color change of phenolphthalein was used as a fast-acting indicator of the pressure. A buffered solution of ammonia, ammonium chloride, and phenolphthalein was adjusted to give a slight pink color at 1 atm, and a portion was placed in the cell. The solution becomes dark red at 1360 atm which shows that the volume change is negative as expected for a reaction of the type[1]

$$\mathrm{HIn} + \mathrm{NH_3} \longrightarrow \mathrm{In^-} + \mathrm{NH_4^+}$$

For the optical cell and sample cell described earlier, with S. A. E. 10W motor oil as the pressurizing fluid, the relaxation time was 8 msec. This time could not be shortened by use of a special fast-acting valve which was held shut by a wire under tension and released by breaking the wire. Faster relaxation can be achieved, however, by using petroleum ether (bp 90–100°) as the pressurizing fluid. We have recently extended the optical path to 2 cm by thinning the quartz windows, and this cell gives relaxation times of 15 msec with oil and 6 msec with petroleum ether. It seems probable that enlargement of the constrictions in the tubing and fittings between the optical cell and reservoir could give relaxation times approaching 1 msec.

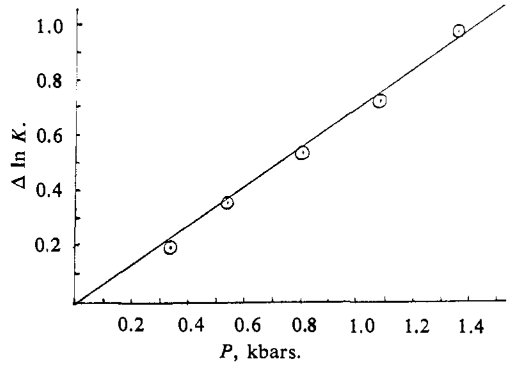

Figure 3. The effect of pressure on the equilibrium constant.

Discussion

Since the accurate measurement of rate constants is antecedent to the determination of activation volumes, we chose for our first trial a fast reaction which had been carefully studied by other methods.[2c,4] The reaction of ferric ion with thiocyanate ion has second-order kinetics, and consequently the relation between the relaxation time and reaction rate constant is

$$1/\tau = k_b + k_f[(\mathrm{Fe^{3+}}) + (\mathrm{SCN^-})] = k_f[(1/K) + (\mathrm{Fe^{3+}}) + (\mathrm{SCN^-})] \quad (2)$$

where k_b and k_f are the backward and forward rate constants, and the quantities in parentheses are the concentrations of uncomplexed ions. The hydrogen ion concentration is still another important variable since Below, Connick, and Coppel[4] found that the normal reaction competes with a base-catalyzed process which would seem to involve $FeOH^{2+}$ as an intermediate. They found that the forward rate at 25° could be represented by eq 3. Wendt and Strehlow[2c]

$$k(\mathrm{sec^{-1}}\ M^{-1}) = 127 + 20.2/(\mathrm{H^+}) \quad (3)$$

report that the two constants have values of 150 ± 50 and 45 ± 4, respectively. Table II gives a comparison of our rate constants at 1 atm with values calculated from eq 3. Except for the second experiment, the agreement is within the range of reproducibility of our measurements of τ. Our data would give values of 115 and 21 for the constants of eq 3.

Table II. Comparison of Measured and Calculated Rates at Normal Pressure

Expt	(Fe^{3+})	(SCN^-)	(H^+)	τ, sec	k (obsd)	k (calcd)
1	0.0070	0.00120	0.200	0.305	223	228
2	0.0148	0.00077	0.400	0.335	135	177
3	0.0148	0.00077	0.100	0.136	325	329
4	0.00163	0.00163	0.200	0.462	214	228
5	0.0072	0.00120	0.800	0.397	164	152
6	0.0072	0.00180	0.800	0.469	139	152

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[5] F. T. Gucker, Jr., *Chem. Rev.*, **13**, 111 (1933).

The effect of pressure on the rate of this reaction is a composite quantity, since the activation volumes for the normal and base-catalyzed paths will be different. It is easily possible to make the latter predominant by using high pH, but it would be impossible to interpret the activation volume since it would include a term of unknown magnitude for the hydrolysis preequilibrium. We therefore concentrated our efforts on the suppression of the base-catalyzed path by using only data from the experiments with pH near zero. Even so, this path contributes 18% and it will be reflected to a corresponding extent in the activation volume.

At 1360 atm with the conditions of expt 5, the relative retardation of rate was 1.35, and at 1080 atm the factor was 1.32. The corresponding activation volumes are +6 and +5 ml according to (4). The activation volume

$$-RT(\partial \ln k/\partial P)_T = \Delta V^* \qquad (4)$$

in this case does not provide a critical test of mechanism, since the measured value is consistent with either a direct bimolecular substitution reaction

$$\mathrm{Fe(H_2O)_6^{3+} + SCN^- \longrightarrow activated\ complex} \qquad (a)$$

or a two-step process involving slow dissocation and rapid combination

$$\mathrm{Fe(H_2O)_6^{3+} \longrightarrow Fe(H_2O)_5^{3+} + H_2O}$$
$$\mathrm{Fe(H_2O)_5^{3+} + SCN^- \longrightarrow Fe(H_2O)_5SCN^{2+}} \qquad (b)$$

A model for eq a is the reaction of N,N,N-trimethylanilinium ion with phenoxide ion ($\Delta V^* = +7$ ml),[6] and models for eq b are the unimolecular decomposition of diazonium ions,[7] *t*-alkylsulfonium ions,[8] alkylmercuric ions,[9] and carboxylate ions[8] ($\Delta V^* = +2$ to $+14$ ml). In the first case the increase of volume results from the neutralization of charge and the release of electrostricted solvent, and in the second case it results from the breakage of a bond.

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Some Perfluoroalkylsulfinyl Halides, $R_fS(O)X$. New Preparations of Trifluoromethylsulfur Trifluoride[1]

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Abstract: The reaction of CF_3SCl with CF_3OF is the superior of four new methods for the preparation of CF_3SF_3. Trifluoromethylsulfinyl fluoride, which is prepared in good yield by the controlled hydrolysis of CF_3SF_3, undergoes metathetical reactions with HX to give new compounds, $CF_3S(O)X$. Trifluoromethylsulfinyl chloride and trifluoromethylsulfinyl bromide are prepared by reactions of $CF_3S(O)F$ with HCl and HBr, respectively. These tend to disproportionate to the respective sulfonyl and sulfenyl halides (R_fSO_2X and R_fSX). The new compound trifluoromethylsulfonyl bromide results from this disproportionation. In the presence of CsF, SOF_2 adds to C_2F_4 and C_3F_6 to give the higher perfluoroalkylsulfinyl analogs, $C_2F_5S(O)F$ and *i*-$C_3F_7S(O)F$.

Trifluoromethylsulfur trifluoride (CF_3SF_3), which was first reported as one of many products resulting from the direct fluorination of CS_2,[2a] more recently has been synthesized in better yield (40–50%) *via* the fluorination of CS_2 or $(CF_3S)_2CS$ with AgF_2.[2b] We wish to report four new methods for the preparation of CF_3SF_3 which involve the fluorination of CF_3SCl or CF_3SSCF_3 with CF_3OF, KF, or F_2. Trifluoromethylsulfur trifluoride is obtained in essentially quantitative amounts from the action of trifluoromethyl hypofluorite on trifluoromethylsulfenyl chloride

$$3CF_3OF + 2CF_3SCl \xrightarrow{-78°} 2CF_3SF_3 + Cl_2 + 3COF_2$$

Potassium fluoride, particularly if present as its carbonyl fluoride or hexafluoroacetone adduct, also fluorinates CF_3SCl to CF_3SF_3 but two-thirds of the CF_3SCl is consumed in the formation of CF_3SSCF_3. Bis(trifluoromethyl) disulfide with CF_3OF or F_2 produces CF_3SF_3 in lower yields accompanied by a variety of other fluorinated compounds.

The perfluoroalkylsulfinyl halides ($R_fS(O)X$) are a new type of compound which have been observed previously only as trace impurities, *e.g.*, $CF_3S(O)F$ in the preparation of CF_3SF_3[2b] and *i*-$C_3F_7S(O)F$ in the preparation of *i*-$C_3F_7SF_3$.[3] The present work deals with the preparation, properties, and some of the reaction chemistry of five perfluoroalkylsulfinyl halides. Trifluoromethylsulfinyl fluoride ($CF_3S(O)F$) is prepared quantitatively *via* the mild hydrolysis of CF_3SF_3

$$CF_3SF_3 + H_2O \longrightarrow CF_3S(O)F + 2HF$$

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(1) Presented in part at the Northwest Regional American Chemical Society Meeting, Richland, Wash., June 1967.

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