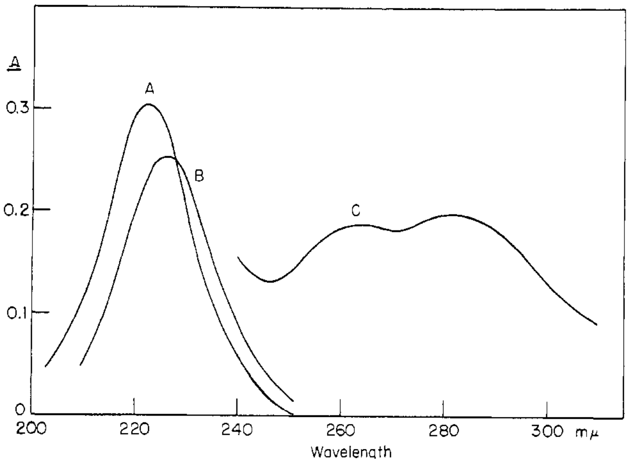

Fig. 2.—Spectra of 2.5 × 10^{-5} *M* Bi(III) in 1-cm. cells: A, in 1 *M* $HClO_4$: B, in 1 *M* $HClO_4$ and 0.45 *M* H_3PO_2; C, as BiI^{-2} in 1 *M* $HClO_4$.

tion is correct, a straight line of unit slope results with an intercept of log β_q.

It should be noticed that the equation only applies to the case of two species being present, both absorbing, and so allows for absorption due to bismuth ions but does not allow for any contribution to the absorbance by iodide ions. It has been verified, by experiment, that iodide does not absorb at this wave length when present at this low concentration.

The plot of the results is shown in Fig. 1, in which the best straight line of unit slope has been drawn. This line agrees very well with the data, confirming that the complex is indeed BiI^{+2}. From the intercept, β_1 was found to be 4.79 × 10^2, in good agreement with the previous method of calculation.

Discussion

A comparison of the results reported here and those reported by previous authors reveals a number of important differences.

The value of the stability constant is tenfold smaller than that reported previously (4.35 × 10^3), which suggests that an error may have been made by previous workers in recording the concentration of iodide. A comparison of the sixth solution in Table I where the iodide concentration was 4.0 × 10^{-5} *M* and a solution in the previous paper where this concentration was given as 3.9 × 10^{-4} *M* reveals approximately the same value for the absorbance.

The failure of previous authors to observe precipitation from the more concentrated bismuth solutions cannot be as readily explained. From the solubility product of bismuth iodide, which has been reported as 8.1 × 10^{-19},[3] one would expect precipitation from some of the solutions in Table I where none appeared and from the solutions prepared by Frolen. We have observed two effects due to the presence of hypohosphorous acid: first, a marked decrease in the *rate* of precipitation of bismuth iodide from supersaturated solutions and, secondly, the formation of a similar-appearing precipitate even in the absence of iodide ions. The latter appears to be mainly metallic bismuth resulting from the reduction of the uncomplexed ion by hypophosphorous acid. Bomberger[7] has, in fact, shown it possible to obtain a quantitative precipitation of metallic bismuth from perchloric acid medium by heating with hypophosphorous acid. It has been our experience that hypophosphorous acid, once opened to the atmosphere, deteriorates rapidly, and this might be the cause of its reactivity having been overlooked.

Experiments have also shown that hypophosphorous acid reacts with dilute solutions of bismuth without precipitation. The absorption band of bismuth is shifted to longer wave lengths and the absorbance is decreased (Fig. 2), suggesting that a weak complex is formed. It was because of this that the second series of measurements of the formation of BiI^{+2} was carried out in the absence of hypophosphorous acid. The good agreement between the results obtained in the two series of experiments, as evidenced by Fig. 1, confirms the suggestion that the complex between bismuth and the acid is very weak. The absorption spectrum of the ion BiI^{+2} has been found to have two peaks above 240 mμ, as shown in Fig. 2, with a maximum absorbance at 282 mμ.

In Fig. 1 the deviation of the lowest result from the line is suggestive of the formation of a second species, presumably BiI_2^+. The narrowness of the range of concentrations which are high enough to permit an appreciable fraction of this species to be formed and still low enough to avoid precipitation of bismuth iodide makes study of this species exceedingly difficult, and no confirmation of its formula or estimate of its formation constant could be made from our data.

Acknowledgments.—This work was supported in part by the United States Atomic Energy Commission under Contract AT(30-1)-905.

(7) D. R. Bomberger, *Anal. Chem.*, **30**, 1321 (1958).

CONTRIBUTION FROM THE MAX PLANCK INSTITUTE
FOR PHYSICAL CHEMISTRY, GOETTINGEN, GERMANY

The Kinetics of the Chromate–Dichromate Reaction as Studied by a Relaxation Method

BY JAMES H. SWINEHART[1a] AND GILBERT W. CASTELLAN[1b]

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In recent years the application of relaxation techniques to the study of fast reactions has received considerable attention. Eigen and deMaeyer[2] have developed the theory and experimental techniques for studying such reactions. However, little attention has been

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(1) (a) Department of Chemistry, University of California, Davis, California; (b) Department of Chemistry, Catholic University of America, Washington, D. C.

(2) M. Eigen and L. deMaeyer, "Techniques of Organic Chemistry," A. Weissberger, Ed., Interscience Publ., New York, N. Y., 1963, Vol. VIII, Part II, Chapter XVIII.

directed toward the simplicity relaxation theory lends to the study of slow reactions.[3] The conditions for using relaxation methods to evaluate the kinetics of a system are the following. First, the system must be in equilibrium. Second, when a perturbation is applied to the system to change the equilibrium, the change must be small enough so that the rate equations can be linearized, that is $\Delta G/RT \ll 1$; then $\mathrm{d}c_i/\mathrm{d}t = -(c_i - \bar{c}_i)/\tau$, where c_i and $\bar{c}_i$ are concentrations of the ith species in the perturbed and the equilibrium state and τ is the relaxation time. The relaxation time is related to the rate constants and concentrations of the species in the equilibrium state established after the perturbation in a unique way depending on the mechanism. In the present communication the authors studied the kinetics of the chromate–dichromate system by a concentration-jump method.

Experimental

Materials.—Solutions were prepared in double-distilled water from potassium dichromate (Merck, reagent) and enough potassium nitrate (Merck, reagent) to make the ionic strength 0.1. Chlorophenol red (Merck) and bromothymol blue (Merck) were used as pH indicators. Indicator solutions were prepared in methanol at 10^{-3} M and diluted to 10^{-5} M with the aqueous solution under study. The pH was adjusted with standard solutions of potassium hydroxide and nitric acid (Fixanal, Hannover, Germany).

Instruments.—Measurements of the percentage transmission of the solutions were made with a Beckman DK-2A spectrophotometer (modified for kinetic studies with a linear time axis) with matched 1-cm. cells. pH measurements were made with a Radiometer 22 pH meter (Radiometer, Copenhagen, Denmark) standardized by commercially available standard buffers.

Procedure.—Experiments were performed by adding enough of a concentrated chromate–dichromate solution B to 3 cc. of chromate–dichromate solution A of known concentration, which contained indicator, to change the total chromium concentration by about 10%. Calculations for this system show the change is well within the limits necessary to allow linearization of the rate equations, in this case $\Delta G/RT \approx 0.008$. Mixing was accomplished by placing solution B in a small plastic sieve with an attached handle so it could be moved up and down quickly in the sample spectrophotometer cell containing 3 cc. of solution A. The sample cell was balanced against a reference cell containing solution A. Thus a difference spectrum was always recorded. The holes in the plastic sieve are small enough so that no solution passes through before mixing begins. Complete mixing is accomplished by several sweeps of the sieve through the cell. The mixing time is about 5 sec. and the volume change on mixing is less than 1%. Observations of the per cent transmission of the indicator in the solution were made as a function of time after mixing. Observations were generally made on the 75–125% or 90–110% transmission scales of the spectrophotometer at 575 mμ for chlorophenol red and 620 mμ for bromothymol blue. The pH change observed spectrophotometrically resulted from the concentration perturbation and was used to calculate the relaxation time, τ. The final pH of the solution, which was used to calculate the concentrations of $HCrO_4^-$, CrO_4^{-2}, and $Cr_2O_7^{-2}$ present, was recorded with a pH meter after the new equilibrium position was reached. The total chromium content was known. The pK of $HCrO_4^-$ was taken[4] as 6.13, and the dimerization constant[5] $[Cr_2O_7^{-2}]/[HCrO_4^-]^2 = 50$.

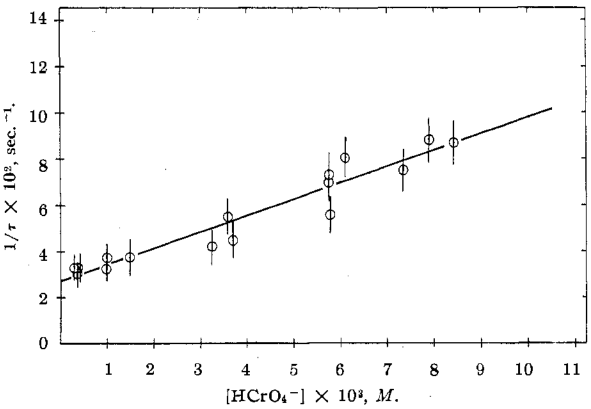

Fig. 1.—Plot of $1/\tau$ *vs.* $[HCrO_4^-]$: ionic strength = 0.1; t = 23°; total initial concentration of Cr was 0.02 M, except at lowest concentration of $HCrO_4^-$ where total Cr was 0.002 M. The pH range of the experiments was between 6.0 and 7.5.

Results and Discussion

The mechanism is assumed to be

$$H^+ + In^- \rightleftharpoons HIn \qquad (1)$$

$$H^+ + CrO_4^{-2} \rightleftharpoons HCrO_4^- \qquad (2)$$

$$2HCrO_4^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} Cr_2O_7^{-2} + H_2O \qquad (3)$$

where In^- and HIn are the deprotonated and protonated forms of the indicator. Steps 1 and 2 are assumed to be fast relative to step 3. This assumption is reasonable since protonation steps are known[2] to be about 10^{10} M^{-1} sec.$^{-1}$. K_1 and K_2 are the association constants for steps 1 and 2. A calculation of the relaxation time of the system using the methods developed by Eigen and deMaeyer[2] yields

$$1/\tau = 4k_{23}[HCrO_4^-]\,\frac{K_2A}{1 + K_2A} + k_{32}\{[H_2O] + [Cr_2O_7^{-2}]\}$$

where

$$A = \left\{[H^+] + [CrO_4^{-2}]\left(\frac{1 + K_1[H^+]}{1 + K_1\{[H^+] + [In^-]\}}\right)\right\}$$

Under the experimental conditions $K_2A \gg 1$ and $[H_2O] \gg [Cr_2O_7^{-2}]$ and these relations remain correct as the total concentration of chromium approaches zero. Thus

$$1/\tau = 4k_{23}[HCrO_4^-] + k_{32}[H_2O]$$

Figure 1 shows a plot of $1/\tau$ *vs.* $[HCrO_4^-]$ at ionic strength 0.1 and temperature 23°. From this plot $k_{23} = 1.8 \pm 0.3$ M^{-1} sec.$^{-1}$ and $k_{32} = 2.7 \pm 0.4 \times 10^{-2}/[H_2O] = 4.9 \pm 0.9 \times 10^{-4}$ M^{-1} sec.$^{-1}$.

The calculated dimerization constant is about 66. This is in fair agreement with the value of 50 used to calculate the concentrations of the various species in the solution. The value of $k_{23} = 1.8$ M^{-1} sec.$^{-1}$ is in good agreement with the value of 1 M^{-1} sec.$^{-1}$ estimated by Schwarzenbach and Meier[5] from neutralization studies. The authors conclude that the proposed mechanism is consistent with the kinetic data. However, other mechanisms are possible and are not eliminated until a more complete study is made.

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(3) G. G. Hammes and R. A. Alberty, *J. Am. Chem. Soc.*, **82**, 1564 (1960), used a relaxation method to study a slow enzymatic reaction.

(4) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants of Metal-ion Complexes, with Solubility Products of Inorganic Substances, Part II," The Chemical Society, London, 1958, p. 29.

(5) G. Schwarzenbach and J. Meier, *J. Inorg. Nucl. Chem.*, **8**, 302 (1958).

The authors believe that the power of the relaxation method, which has been widely applied to very fast reactions, is well illustrated by the application to the slow chromate–dichromate system. In many cases the technique has significant experimental advantages over various other methods. The simplification in interpretation, particularly for complex reactions, is enormous.

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CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY,
INORGANIC RESEARCH DEPARTMENT, ST. LOUIS 66, MISSOURI

Nuclear Magnetic Resonance Studies of $P_2O_3Cl_2F_2$ and Its Reorganization Products

BY M. M. CRUTCHFIELD, C. F. CALLIS AND J. R. VAN WAZER

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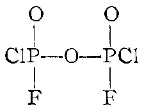
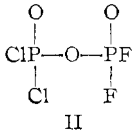
Preliminary P^{31} n.m.r. measurements made in our laboratory on a compound of empirical formula $P_2O_3Cl_2F_2$ identified it as the symmetrical compound diphosphoryl difluoride dichloride



$$\overset{O}{\underset{F}{ClP}}—O—\overset{O}{\underset{F}{PCl}}$$

I

although details of spectral fine structure remained unexplained.[1] Subsequent heating in a sealed tube at 50° for several days led to the slow growth of reorganization products which were detected by the appearance of additional peaks in the 24.3 Mc. P^{31} spectrum. Under low resolution, the growth of an apparent 1:2:1 triplet with coupling constants appropriate for P–F bonds (*ca.* 1100 c.p.s.) suggested the formation of some of the asymmetrical isomer



$$\overset{O}{\underset{Cl}{ClP}}—O—\overset{O}{\underset{F}{PF}}$$

II

by halogen interchange.[2] The total spectrum was incompatible with the presence of a compound of this structure, however, since no additional P^{31} resonance peaks attributable to the chlorine-bonded phosphorus were observed and the separations of the apparent triplet peaks were not quite equal.

TABLE I

N.M.R. DATA FOR REORGANIZATION PRODUCTS OF $P_2O_3Cl_2F_2$

Fluorine spectra

Peaks	F^{19} chem. shift p.p.m. from CF_3COOH 40.0 Mc.	24.3 Mc.	P–F coupling $\lvert J_{P_1F_1}\rvert = \lvert J_{P_2F_2}\rvert$, c.p.s. 40.0 Mc.	24.3 Mc.	Assignment
A	−41.0	−41.8	1121	1123	$\overset{O}{\underset{Cl}{FPO}}$— end groups
B	−70.2	−70.2	1172	1177	$P(O)Cl_2F$ neso groups
C	−9.8	−10.1	1046	1060	—$\overset{O}{\underset{F}{OPO}}$— middle groups

Phosphorus spectra

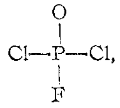
Peaks	P^{31} chem. shift p.p.m. from H_3PO_4 24.3 Mc.	16.2 Mc.	P–F coupling $\lvert J_{P_1F_1}\rvert = \lvert J_{P_2F_2}\rvert$, c.p.s. 24.3 Mc.	16.2 Mc.	Assignment
A	+19.0	+18.5	1116	1125	$\overset{O}{\underset{Cl}{FPO}}$— end groups
B	−0.8	−1.7	1190	1175	$P(O)Cl_2F$ neso groups
C	+44.0	+43.9	1057	1040	—$\overset{O}{\underset{F}{OPO}}$— middle groups

Average for all frequencies

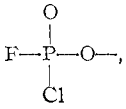
	$\lvert J_{PF}\rvert$, c.p.s.	Std. dev., c.p.s.
A	1121	4
B	1179	8
C	1050	9

To resolve these apparent anomalies, additional P^{31} n.m.r. spectra have been taken at both 24.3 and 16.2 Mc., as well as F^{19} n.m.r. spectra at 40.0 and 24.3 Mc. Also, a double irradiation experiment[3] was performed in which the P^{31} spectrum was observed at 16.2 Mc., while simultaneously exciting the fluorine resonance at 37.6 Mc., in order to simplify the spin–spin interaction between phosphorus and fluorine.

The results of these experiments, summarized in Fig. 1 and Table I, demonstrate conclusively that the sealed tube reorganization of I at 50° (in the presence of possible catalytic traces of water) results not in fluorine redistribution but in the breaking of P–O–P bonds to form phosphoryl and polyphosphoryl halides containing, preferentially, one P–F bond per phosphorus. The P^{31} and F^{19} chemical shifts of the reorganization mixture at the four radiofrequencies can only be interpreted as arising from neso, end, and middle phosphoryl halide groups of the types

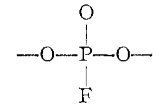


$$Cl—\overset{O}{\underset{F}{P}}—Cl,$$



$$F—\overset{O}{\underset{Cl}{P}}—O—,$$

and



$$—O—\overset{O}{\underset{F}{P}}—O—$$

respectively. If halogens are also undergoing positional exchange, the thermodynamics must be biased in favor of monofluoro substitution, since no trace of a signal from any $-P(O)F_2$ group could be detected in the phosphorus spectra. What previously appeared as an apparent large triplet in the 24.3 Mc. P^{31} spectrum

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[1] C. Stolzer and A. Simon, *Chem. Ber.*, **94**, 1976 (1961).

[2] L. C. D. Groenweghe and J. H. Payne, Jr., *J. Am. Chem. Soc.*, **81**, 6357 (1959).

[3] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, p. 160.