than with oxonine. No concentration of the dye could be reached high enough to preserve the homogeneity of the solution during the experiment and yet to raise the change in magnetic pull during the reduction above the limits of error of the method in its present state. Thus the magnetic measurement with thionine in alkaline solution at least confirms the result obtained potentiometrically, that the semiquinone formation constant is distinctly smaller than for oxonine, but no quantitative result could be obtained.

Summary

A differential magnetometric method is described by which the development of a semiquinone radical on partial reduction of organic dyestuffs can be recognized owing to the increment of susceptibility caused by the free radical. In some cases the difference in susceptibility is measured before and after adding the reducing agent (ascorbic acid), namely, in strongly acid solution of thiazine dyestuffs. In other cases the method of slow reduction is used, for example, in alkaline solution of oxonine, where glucose is added at the beginning, and the change of susceptibility is measured during the slowly progressing reduction. In the case of oxonine, the paramagnetic increment passes through a maximum.

The maximum concentrations of the free radical, calculated from the magnetic data, agree fairly well with those values previously obtained by the potentiometric method. In addition the data show that for the dyestuffs examined here no noticeable dimerization of the radicals takes place although the concentrations of the dyes are more than a hundred times higher than in the potentiometric experiments formerly described.

The Exchange Reaction between Chloride Ion and Tertiary Butyl Chloride

BY WALTER KOSKOSKI,* HOWARD THOMAS AND ROBERT DUDLEY FOWLER

Introduction

Several ionization mechanisms have been studied by the method of radioactive indicators. Tuck[1] measured the rate of electrolytic dissociation of t-butyl iodide in sulfur dioxide solution and Nevell, de Salas and Wilson[2] studied exchanges in camphene hydrochloride. The latter case is of considerable interest since solvent effects and the effect of heavy metal chlorides[3] indicate that the ionization is the rate controlling step in the isomerization of camphene hydrochloride to isobornyl chloride. However, the exchange work was reported to indicate that the ionization as measured by radio chlorine exchanges was much too rapid to be the rate controlling step. Prior to any possible detailed investigation into the camphene hydrochloride exchanges it was decided to study exchanges in a similar but simpler compound. The similarities in the reactivities of t-butyl chloride and camphene hydrochloride have

been pointed out by Meerwein and van Emster[3] so t-butyl chloride was chosen as an interesting compound in which to study exchanges. Formic acid was chosen as the solvent since the rate of hydrolysis[4] of t-butyl chloride has been studied in this solvent and it offers a convenient check of the exchange work.

Experimental

Materials.—t-Butyl chloride was prepared from t-butyl alcohol and concentrated hydrochloric acid. It was distilled and then redistilled from phosphorus pentoxide and the fraction boiling at 49.7° (742.4 mm.) was used. The formic acid was distilled from anhydrous copper sulfate and then further purified by repeated fractional freezing until the freezing point (8.4°) no longer changed. Solutions of the butyl chloride in formic acid were standardized by permitting a measured amount to hydrolyze overnight in water and then titrating the resulting chloride by the Volhard method. Preliminary experiments with weighed amounts of butyl chloride indicated that this was a satisfactory method for standardizing the organic chloride solutions. The radio-chlorine was prepared by bombarding chloroform with neutrons from the deuteron–deuteron disintegration apparatus in this Laboratory. After irradiation the active chloride was removed from the chloroform by shaking with water containing a little

* This work constitutes a portion of a thesis to be submitted by W. Koskoski in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Johns Hopkins University.

(1) J. L. Tuck, Trans. Faraday Soc., 34, 222 (1938).

(2) T. P. Nevell, E. de Salas and C. L. Wilson, J. Chem. Soc., 1188 (1939).

(3) Meerwein and van Emster, Ber., 53, 1815 (1920).

(4) L. C. Bateman and E. D. Hughes, J. Chem. Soc., 1187 (1937).

lithium chloride. The aqueous solution was then evaporated to dryness, the vessel was swept out with dry nitrogen, and the dry lithium chloride was taken up with formic acid directly from the freezing vessel.

Procedure.—The exchanges were carried on in single reaction vessels and also in Y-shaped sealed vessels. The radio-chlorine solution was placed in one arm, the butyl chloride in the other and the vessels were sealed and placed in a thermostat at 15°. When they attained thermal equilibrium, they were inverted and shaken. After suitable times the vessels were broken and the contents plunged into 25 cc. of cold ether. In the case of the single reaction vessels the samples were pipetted into the cold ether. The chloride ions were extracted by two successive extractions with equal volumes of water. The chloride ions were then precipitated with excess silver nitrate and the filtrate was analyzed for excess silver ion. The silver chloride precipitates were collected on 2.5-cm. filter papers in a Hirsch funnel, washed with water and acetone, dried, mounted and examined for activity. The decay curves were followed up for several half lives and then were all extrapolated to a common time. The counter tubes and circuits were the same as those used in our previous work.[5]

Treatment of Results

Bateman and Hughes[4] have shown that when t-butyl chloride is placed in dry formic acid an equilibrium is established rapidly between the butyl chloride, chloride ions and isobutylene. In view of this fact one would expect the exchange to go through the equilibrium

$$\text{RCl} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{R}^+ + \text{Cl}^- \quad (1)$$
$$\text{olefin} + \text{H}^+$$
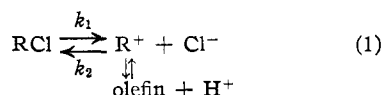
The values k_1 and k_2 can be found for the exchanges and the k_1 value should be the same as the rate constant for the hydrolysis since ionization is the rate controlling step in the hydrolysis. If a is the initial activity and x is the activity in the organic chloride, the rate of appearance of activity in the t-butyl chloride will be

$$dx/dt = k_2[\text{R}^+][\text{Cl}^{*-}] - k_1[\text{RCl}^*] \quad (2)$$

for our purpose we may equate $k_2[\text{R}^+] = k_3$ and we get

$$dx/dt = k_3 a - x(k_3 + k_1) \quad (3)$$

integrating

$$(k_3 + k_1) = \frac{2.3}{t} \log \frac{1}{1 - \frac{x}{a} - \frac{x}{a}\frac{k_1}{k_3}} \quad (4)$$

By permitting the exchange to come to equilibrium the ratio k_1/k_3 can be obtained and the values of both constants can be evaluated.

Discussion of Results

Table I gives the results of a typical exchange

(5) W. Koskoski, R. W. Dodson and R. D. Fowler, THIS JOURNAL, **63**, 2149 (1941).

run made in dry formic acid. The equilibrium concentrations of t-butyl chloride and chloride ion were 0.255 M and 0.0256 M, respectively. The constant $(k_3 + k_1)$ was calculated from equation (4).

TABLE I

$t_{sec.}$	x/a	$(k_3 + k_1) \times 10^3$
110	0.247	2.9
237	.449	2.9
370	.586	2.8
592	.763	3.1
∞	.904	

The value for infinite time was obtained by permitting the reaction to run for about two hours. This value was checked in other runs made under very similar conditions and the same result was obtained to within experimental error (which may be somewhat larger than in the other measurements since here comparatively feeble radioactive samples were measured). Since the sum and the ratio of k_1 and k_3 were known, the value k_1 was evaluated and found to be 0.0003 sec.$^{-1}$. This constant should be a measure of ionization if ionization is occurring and therefore should check with the constant for the rate of hydrolysis in formic acid since ionization is considered to be the rate determining step. The hydrolysis constant as reported by Hughes and Bateman[4] is 3.7 $\times$ 10^{-4} sec.$^{-1}$. Our exchange constant is 3 $\times$ 10^{-4} sec.$^{-1}$. The agreement is good considering the experimental error. No attempt was made to determine the order of the reaction with respect to R$^+$ since it was shown by Ingold[6] in the study of the intervention of azide ion in the hydrolysis of t-butyl bromide that the reaction between R$^+$ and the azide ion was bimolecular. This reaction is closely analogous to the one involved here and it is safe to assume the exchange is bimolecular with respect to R$^+$ and Cl^{*-}. However, it is of interest to study the exchange in the presence of hydrolysis for two reasons: (1) if there is any appreciable exchange due to a bimolecular collision between t-butyl chloride and radio chloride ion, one should observe a maximum in the plot of the amount of exchange against time as was the case in the bromide exchange in α-bromopropionic acid[5]; (2) if there is an appreciable amount of reassociation in the reaction

$$\text{RCl} \overset{\text{H}_2\text{O}}{\underset{}{\rightleftarrows}} \text{R}^+ + \text{Cl}^- \longrightarrow \text{ROH}$$
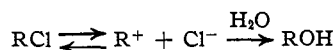
it would be detected. With these two considera-

(6) L. C. Bateman, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 960 (1940).

tions in mind an exchange run was made with 0.196 M butyl chloride in formic acid containing 10% water by volume. The results are given in Table II where r is the ratio of the activity in the chloride ion to that in the control.

TABLE II

$t_{sec.}$	r	Cl⁻
281	0.94	0.022
600	.94	.042
902	.96	.061
1283	1.02	.078

It is apparent that to within experimental error there is no exchange, indicating that there is no appreciable exchange due to a bimolecular collision between the butyl chloride and chloride ion and that there is no appreciable reassociation[6] during the course of hydrolysis.

Summary

Exchanges between radio-chloride ion and t-butyl chloride have been studied in formic acid and it was found that the exchange proceeded through the equilibrium established between butyl chloride, isobutylene and chloride ions. There was no appreciable contribution to the exchange from a bimolecular collision between butyl chloride and chloride ion. The constant corresponding to rate of ionization was found to be in good agreement with the constant for the rate of hydrolysis under similar conditions.


II. Chain Reactions of Ozone in Aqueous Solution. The Interaction of Ozone and Formic Acid in Aqueous Solution

BY HENRY TAUBE

In a previous article[1] experimental results on the reaction between ozone and hydrogen peroxide and the catalytic decomposition of ozone induced by this reaction were shown to be consistent with a mechanism involving the free radicals HO and HO_2 as intermediates. It was also found that other reducing agents (formic acid,[2] certain metal ions) also catalyze the decomposition of ozone. In this paper more detailed experimental results on the interaction of ozone and formic acid are presented, and the results are correlated with those obtained in the ozone–peroxide system.

Two equations[3] are necessary and sufficient to express the stoichiometric results

$$HCOOH + O_3 = CO_2 + O_2 + H_2O \quad (A)$$
$$2O_3 = 3O_2 \quad (B)$$
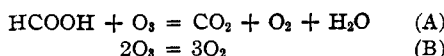
No evidence was found for oxidation of formic acid by oxygen; even when the ratio of $(HCOOH)/(O_3)$ was as high as ten, the corresponding consumption ratio was less than unity. Neither peroxides nor oxalic acid could be detected as end-products of the reaction.

It was found convenient to represent the rates by the following differential equations

$$\frac{-d(HCOOH)}{dt} = k_A(HCOOH)(O_3)$$

and

$$-\left[\frac{d(O_3)}{dt} - \frac{d(HCOOH)}{dt}\right] = k_B(O_3)^2$$

where k_A and k_B[4] are not constants. k_A was calculated from the measured concentrations of formic acid by using the approximate equation

$$k_A = \frac{2.3}{\overline{(O_3)}\ t} \log \frac{(HCOOH)_0}{(HCOOH)_t}$$

where

$$\overline{(O_3)} = \frac{(O_3)_0 + (O_3)_t}{2}$$

k_B was calculated from the expression

$$k_B = \frac{\Delta B}{(O_3)_0(O_3)_t\ t}$$
$$\Delta B = \Delta(O_3) - \Delta(HCOOH)$$

Materials.—Formic acid solutions were prepared by acidifying c. p. sodium formate with perchloric acid solution.

The solutions of ozone in dilute perchloric acid were pre-

(1) Taube and Bray, THIS JOURNAL, **62**, 3357–73 (1940).

(2) Ref. 1, p. 3366.

(3) Analogous reactions in the peroxide–ozone and the formic acid–ozone systems are given the same numbers. Arrows are used throughout to represent rate-determining steps.

(4) This definition of k_B differs from that used in the published experiments, ref. 1, p. 3366, and may be converted by multiplying by the factor $(HCOOH)/(O_3)$. When expressed in the same units, the published results agree with the present ones to within 5–10%.