

phenyl group whereas the xanthyl group has a greater effect than two phenyl groups.<sup>2</sup> Thus one would expect that the ketone *p*-chlorobenzophenone would have a greater tendency while xanthone would have a lesser tendency to form double waves in basic media than benzophenone.

These two ketones have been studied in 25% ethanol-water media over a *pH* range of about 1 to 13. The results listed in Table I were in accord with those expected. *p*-Chlorobenzophenone gives the usual two waves in acid media, these merging at a *pH* between 4.7 and 5.6.<sup>3</sup> The potential of this single wave decreases to  $-1.52$  as the *pH* is increased to 12.8. A small second wave of half-wave potential  $-1.61$  was first observed at a *pH* of 7.5. The potential of this wave had decreased to  $-1.74$  v. at a *pH* of 11.2. The wave was not present in 0.1 *M* NaOH (ketone concentration  $2.5 \times 10^{-4}$  *M*) but did appear when the base concentration was reduced to  $1 \times 10^{-3}$  *M*. Benzophenone at the same concentration gave only one wave in these same basic solutions.<sup>1</sup>

TABLE I

$E_{1/2}$  vs. THE SATURATED CALOMEL ELECTRODE (ALL  $E_{1/2}$  VALUES ARE NEGATIVE)

<i>pH</i> (aq.)	<i>pH</i> (alc.)	$E_{1/2}^1$	$E_{1/2}^2$	$E_{1/2}^{12}$ <sup>a</sup>	$E_{1/2}^4$	Total curr., μa.
<i>p</i> -Chlorobenzophenone <sup>b</sup>						
1.1	1.4	0.89	..	..	..	0.75
2.7	3.1	0.93	1.15	..	..	1.39
4.7	5.1	1.07	1.26	..	..	1.57
5.6	6.0	..	..	1.26	..	1.57
7.5	8.0	..	..	1.36	1.61	1.52
8.5	9.1	..	..	1.41	1.70	1.63
9.6	10.2	..	..	1.45	1.74	1.66
11.2	11.5	..	..	1.49	1.77	1.28
12.8	12.8	..	..	1.52	..	1.05
Xanthone <sup>c</sup>						
1.0	1.3	0.84	..	..	..	0.44
2.7	3.2	0.99	..	..	..	.47
3.7	4.1	1.05	..	..	..	.42
4.7	5.2	..	..	1.21	..	1.12
5.6	6.2	..	..	1.23	..	0.92
6.7	7.2	..	..	1.26	..	.90
7.6	8.0	..	..	1.29	..	.83
8.6	9.0	..	..	1.37	..	.88
9.6	10.1	..	..	1.43	..	.59
12.7	12.7	..	..	1.45	..	.45

<sup>a</sup> Indicates  $E_{1/2}$  of wave formed by merging waves 1 and 2.  
<sup>b</sup> Concentration of ketone 0.000250 *M*. <sup>c</sup> Concentration of ketone 0.000156 *M*.

In the case of xanthone, only one wave was observed over the entire *pH* range. There was a slight indication of separation of the two acid waves at a *pH* of 5.2. Considerably higher currents were observed between a *pH* of about 5 to 9 than at lower or higher *pH* values. A few runs were also made in dilute sodium hydroxide solutions. At a ketone concentration of  $1.56 \times 10^{-4}$  *M* and NaOH concentration of  $1 \times 10^{-4}$  *M* no indication of a second wave could be seen. Since benzophenone

also gave only one wave under these conditions some runs were made at higher ketone concentrations. It was necessary to use 50% ethanol to keep xanthone from precipitating. At ketone concentrations of  $8 \times 10^{-4}$  to  $1.25 \times 10^{-3}$  *M* in 50% ethanol a second wave could be definitely seen with benzophenone, whereas there was only a slight indication of a second wave with xanthone.

### Experimental

The current-voltage curves were determined with a Leeds and Northrup Electro-Chemograph Type E. The instrument was normally operated at a damping of 3, the half-wave potentials being corrected by 0.056 v. for lag at this damping. The electrolysis cell, buffer solution and experimental procedure were the same as previously described.<sup>1</sup>

A single capillary of Corning Marine barometer tubing was used. Its characteristics were: droptime 5.0 sec.,  $m = 1.858$  mg./sec., determined in 25% ethanol at a *pH* of 5.5 and  $-1.00$  v. The resistance of the cell was measured at several *pH* values and a correction for *IR* drop was made when this amounted to as much as 0.01 v.

All cell solutions were 25% by volume of 95% ethanol unless otherwise indicated. The two ketones were commercial products, purified by recrystallization. Melting points (uncor.) were: *p*-chlorobenzophenone 72–73°, xanthone 173–174°. Cell solutions of *p*-chlorobenzophenone were  $2.5 \times 10^{-4}$  *M*, those of xanthone  $1.56 \times 10^{-4}$  *M*. More concentrated solutions of the latter ketone gave precipitation when mixed with basic buffers.

Measurements of *pH* were made using a glass electrode and a Beckman model H-2 *pH* meter. A high *pH* glass electrode was used in basic media.

All experiments were run at room temperature, which was normally between 23 and 28°.

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### The Rate of Deuterium Exchange between Ethanol and Water. A Reinvestigation<sup>1</sup>

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Orr has reported that the establishment of equilibrium between ethanol and heavy water is a reaction of measurable rate, having a half-time of about four hours at 25°.<sup>2</sup> Orr mixed samples of heavy water (about 10% D) with somewhat smaller volumes of ethanol and after an allotted time added anhydrous calcium sulfate. The calcium sulfate was removed, air-dried of the adherent ethanol and dehydrated at 150° in vacuum. The composition of the resultant mixture (containing light and heavy water and < 0.4% ethanol) was measured by determination of the density and of the refractive index (using an interferometer).

On the other hand, Jungers and Bonhoeffer found that the equilibrium between ethanol and heavy water is established too rapidly to measure.<sup>3</sup> These workers, however, separated their aqueous ethanol solutions by extraction with benzene.

Since the validity of the widely-held belief that all proton transfer reactions between oxygen atoms occur too rapidly to measure (by con-

(1) This study was carried out as part of a project sponsored by the Atomic Energy Commission.

(2) W. J. C. Orr, *Trans. Faraday Soc.*, **32**, 1033 (1936).

(3) J. C. Jungers and K. F. Bonhoeffer, *Z. physik. Chem.*, **A177**, 480 (1936).

(2) H. Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 591.

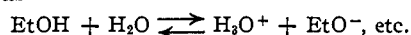
(3) All *pH* values herein are of the aqueous buffer.

ventional means, at least) is of considerable importance in relation to the theory that in reactions subject to general acid and/or base catalysis the rate-controlling step is a proton transfer,<sup>4</sup> and also in relation to learning what compounds are *primary* acids and bases in the Lewis sense,<sup>5</sup> it was felt that another check of Orr's work, using his method for separating water from ethanol, would be desirable.<sup>6</sup> However, in order that the final concentration of deuterium in the water should differ more significantly from that used originally, a larger amount of ethanol relative to water, and a higher concentration of heavy water were used in our experiments, of which the following procedure is an example:

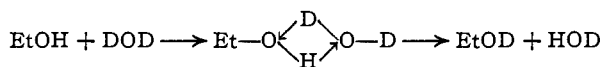
To 3.2 ml. of absolute ethanol at 0° was added 1.0 ml. of water (17.1 atom % deuterium) at about 0.5°. The mixture was shaken until homogeneous (5 seconds), poured onto 10 g. of anhydrous calcium sulfate, shaken for five minutes, and evacuated to 8 mm. pressure for 2.5 hours to remove the ethanol (all at 0°). The water was removed by heating to 197° under 8 mm. pressure, its ethanol content determined by the method of Williams and Reese<sup>7</sup> and its density by the falling drop method of Roseburg and Van Heyningen.<sup>8</sup> From the density and a correction for the 0.0087 g./ml. ethanol (based on the assumption that its partial molal volume is not affected by the deuterium content of the solvent), the water was shown to contain 9.0 atom % deuterium (11.3% would correspond to random distribution).

In another experiment at 0°, 9.4% deuterium (*vs.* 11.3% if random) was found and in a run at room temperature (*ca.* 34°) 10.1% deuterium (*vs.* 11.4% for random distribution) was found.

While we believe we have shown that the prototropic equilibrium between water and the hydroxy group of ethanol is established too rapidly to measure under our conditions, this does not establish any minimum for the rate of reactions such as



which accomplish a net proton transfer, since the unshared electron pairs on oxygen make feasible<sup>9</sup> the establishment of this equilibrium by proton-exchange reactions by mechanisms of the type shown below in which ions play no part.



It seems possible that the results of Orr are fortuitous. In no case would an error of more than 0.4 mg. in weighing his pycnometer be necessary to make his results correspond to purely random distribution of deuterium between the hydroxy group of the ethanol and water. From the facts that his weights are given to the nearest 0.1 mg., and that no contrary statement is made, it seems likely that he used an ordinary analytical balance

(4) R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, 1941, chap. VII; L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 241.

(5) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938); G. N. Lewis, and G. T. Seaborg, *This Journal*, **61**, 1886 (1939).

(6) Since this problem was begun, we have learned from a private communication that Dr. H. Kwart of the University of Delaware has found the deuterium exchange between methanol and water to be too rapid to measure under similar conditions.

(7) M. B. Williams and H. D. Reese, *Anal. Chem.*, **22**, 1556 (1950).

(8) F. Roseburg and W. E. Van Heyningen, *Ind. Eng. Chem., Anal. Ed.*, **14**, 363 (1942).

(9) See A. J. Brodskii and L. V. Sulima, *Doklady Akad. Nauk S. S. R.*, **74**, 513 (1950).

on which the error of weighing (plus all of the other errors in the determination, such as that in filling the pycnometer) might reasonably have this magnitude.

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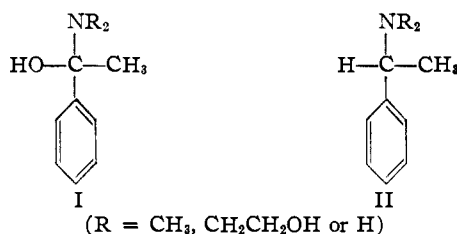
### Extension of the Willgerodt Reaction

BY RICHARD T. GERRY AND ELLIS V. BROWN

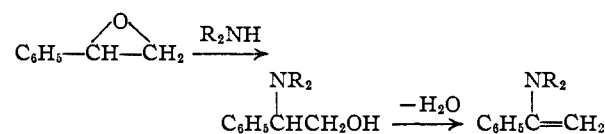
RECEIVED JULY 2, 1952

Recent papers have shown that the scope of the Willgerodt reaction is considerably broader than had previously been supposed. Several investigators<sup>1,2</sup> have reported successful Willgerodt reactions with olefins, carbinols, thiols and acetylenes.

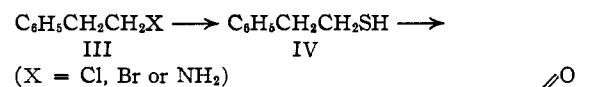
We feel that further extensions of the Willgerodt reaction may be of assistance in elucidating the mechanisms of this reaction as proposed by King and McMillan<sup>1</sup> and Carmack and DeTar.<sup>2</sup> The intermediates proposed by these workers are in many cases too reactive to be isolated by the usual preparative methods. However, the behavior of more stable but closely related compounds may be of interest. For example, Carmack and DeTar postulated a hydramine intermediate (I) in their reaction sequence. We have tested three amines (II) of somewhat related structure.



Styrene oxide was also investigated since it could conceivably go through the following steps to yield another intermediate of Carmack and DeTar.



Again, compounds of type III would be expected to follow the sequence of King and McMillan. This is possible since the yields of amides from



these compounds are only slightly lower than that reported for 2-phenylethanethiol (IV).

If either mechanism is applied to  $\beta$ -bromostyrene the amides might be formed in fewer steps than from styrene itself. Styrene yielded 71% of phenylacetamide while bromostyrene, under comparable conditions, gave 80% yield of this amide.

(1) J. A. King and F. H. McMillan, *This Journal*, **68**, 525, 632 (1946).

(2) M. Carmack and D. F. DeTar, *ibid.*, **68**, 2029 (1946).