

TABLE I
 EXPERIMENTAL RESULTS

Compound	Catalyst No. 1 Cr ₂ O ₃ on CrO ₃ , 15 g. Gas			Catalyst No. 2 Al ₂ O ₃ on Cr ₂ O ₃ , 12 g. Gas			Catalyst No. 3 Cr ₂ O ₃ on Al ₂ O ₃ , 30 g. Gas			Catalyst No. 4 Mo ₂ O ₃ on Al ₂ O ₃ , 30 g. Gas			Catalyst No. 5 V ₂ O ₅ on Al ₂ O ₃ , 30 g. Gas		
	Vol. % Olef.	Arom.	0-6 hr. cc./min.	Vol. % Olef.	Arom.	0-6 hr. cc./min.	Vol. % Olef.	Arom.	0-6 hr. cc./min.	Vol. % Olef.	Arom.	0-6 hr. cc./min.	Vol. % Olef.	Arom.	0-6 hr. cc./min.
<i>n</i> -Heptane	14	18	28 to 11	10	13	15 to 8	16	11	14 (constant)	9	20	48 to 20	10	1	2 to 6
<i>n</i> -Heptane	15	16	19 to 9	10	11	14 to 7	15	17	14	9	24	41 to 20	10	1	3 to 5
<i>n</i> -Heptane	14	16	24 to 7	10	11	15 to 8	15	13	13	10	23	36 to 27	11	9	4 to 10
2,2,4-Trimethyl- pentane	19	- 3	6 to 2	14	- 2	5 to 2	18	- 1	4	9	3	19 to 10	15	-3	2 to 3
2,2,4-Trimethyl- pentane	19	- 1	6 to 2	16	- 2	4 to 3	18	- 1	4	11	1	15 to 8	18	-6	2 to 5

tained by depositing alumina on chromium oxide.

The behavior of molybdenum oxide on alumina is different. Aromatics are definitely formed from 2,2,4-trimethylpentane, while the olefin content is the same from both *n*-heptane and 2,2,4-trimethylpentane.

Further work is in progress on the determination of isomerization properties of aromatizing catalysts at higher temperatures.

We wish to thank Professor Hugh S. Taylor for advice and interest in this investigation.

Conclusions

1. Chromium oxide unsupported, chromium

oxide on alumina, alumina on chromium oxide, vanadium oxide on alumina do not aromatize 2,2,4-trimethylpentane at 475°.

2. Molybdenum oxide on alumina at 475° gives small but definite amounts of aromatics from 2,2,4-trimethylpentane, indicating isomerizing properties of this cyclizing catalyst.

3. Olefin production from *n*-heptane and 2,2,4-trimethylpentane on aromatizing isomerizing catalyst is the same, while on aromatizing non-isomerizing catalyst, 2,2,4-trimethylpentane yields more olefins than *n*-heptane.

PRINCETON, N. J.

RECEIVED NOVEMBER 29, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY AND THE DEPARTMENT OF PHYSIOLOGY OF THE MEDICAL SCHOOL OF THE UNIVERSITY OF MINNESOTA]

The Reduction of Cystine at the Dropping Mercury Electrode¹

BY I. M. KOLTHOFF AND CYRUS BARNUM

In a previous paper² the anodic current-voltage curves obtained with cysteine at the dropping mercury electrode have been presented and discussed. The most important conclusion arrived at was that cysteine is not oxidized to cystine at the dropping electrode but that it depolarizes the electrode with the formation of mercurous cysteinate, HgSR. In the present paper the reduction waves obtained with cystine (denoted in the following as RSSR) at the dropping electrode are presented and discussed. The reduction of cystine at the dropping mercury electrode has received little attention from workers in the field of polarography. Brdicka³ found that when cystine was electrolyzed in a buffer solution of 0.1 *N* ammonium chloride and 0.1 *N* ammonia he

obtained a polarographic wave, the height of which was proportional to the concentration of cystine, and he inferred that the reduction involved two electrons. Brdicka further found the "reduction potential" (depolarization potential) of 0.005 *M* cystine in 1 *N* hydrochloric acid to be -0.37 volt (*vs.* N. C. E.) and in 1 *N* sodium hydroxide to be -1.15 volts. From the difference of 0.78 volt Brdicka concluded that the dependence of the reduction potential upon the *pH* of the solution was in accord with the thermodynamically reversible reduction of cystine to cysteine. Considering that cystine has both weakly acid and basic functions this relation would not be expected to be fulfilled over such a wide range of *pH* values as from 0 to 14. Brdicka's results do not indicate that the reduction of cystine at the dropping electrode is reversible in a thermodynamic sense. A somewhat more detailed study was made by Roncato.⁴ He studied

(1) From a thesis submitted to the Graduate School of the University of Minnesota by Cyrus Barnum in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1940.

(2) I. M. Kolthoff and Cyrus Barnum, *THIS JOURNAL*, **62**, 3061 (1940).

(3) R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **5**, 238 (1933).

(4) A. Roncato, *Arch. sci. biol.*, **20**, 146 (1934).

the polarographic reduction of cystine in unbuffered neutral, acid and alkaline solutions of lithium chloride. In strongly acid solution he found a single wave with a pronounced maximum while in neutral solution he found a wave clearly showing two steps. The first step was attributed by him to a reversible reduction of cystine to cysteine, while the second step, which follows the first one fluently (the latter being without a range of constant current) was considered by him to be due to an irreversible reduction of cystine. He concluded that the reversible step represented the reduction of the cystine cation while the irreversible step was due to neutral cystine or to the cystine anion. It should be mentioned that Roncato's waves cannot be subjected to an exact analysis since his solutions were unbuffered⁵ and the reduction potential depends upon the *pH*, $\text{RSSR} + 2\text{H}^+ + 2e \rightarrow 2\text{RSH}$, as shown already by Brdicka. In our experiments we worked in buffered solutions and found an apparent two step reduction over a certain *pH* range. Our interpretation of the phenomenon, however, is quite different from that of Roncato. The cystine waves have peculiar characteristics and their interpretation is quite involved as is shown below.

Experimental

Materials Used.—Cystine, c. p., was purchased from Pfanstiehl and contained 0.1% ash.

Circuit and Apparatus.—These were the same as described in a previous paper.² The temperature was maintained at $25.0 \pm 0.1^\circ$ throughout all the experiments.

Experimental Results

Curve I in Fig. 1 shows the current-voltage curve (hereafter to be referred to as c. v. curve) of 0.001 *M* cystine in 0.1 *N* hydrochloric acid. It is seen that a pronounced maximum occurs in the curve but that at -0.7 volt (*vs.* S. C. E.) the diffusion current has been reached. Neither polyvalent cations (La^{+++}) nor polyvalent anions (ferrocyanide⁼) were able to suppress the maximum. It could be suppressed, however, by the addition of capillary active substances such as gelatin, phenol, resorcinol, thymol, methylene blue, methyl red or camphor. The effect of these substances is very interesting; they not only eliminate the maximum but also displace the reduction wave to more negative potentials.

(5) O. H. Müller, *Chem. Rev.*, **24**, 95 (1939).

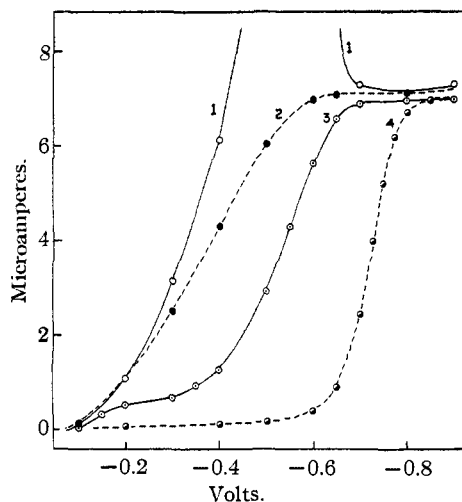


Fig. 1.—Effect of thymol on the curve of 0.001 *M* cystine in 0.1 *N* hydrochloric acid: (1) no thymol (maximum reached at 20.35 microamperes); (2) 2.4×10^{-5} *M*; (3) 1.2×10^{-4} *M*; (4) 4.8×10^{-4} *M*.

Thymol was found to be the best agent for suppressing the cystine maxima. Curve 2 in Fig. 1 shows the c. v. curve of 0.001 *M* cystine in 0.1 *N* hydrochloric acid after the solution had been made 2.4×10^{-5} *M* to thymol. This was found to be the minimal concentration of thymol which would suppress the maximum. It is further seen in Fig. 1 that higher concentrations of thymol shift the cystine reduction wave to increasingly more negative potentials.

Gelatin also displaces the reduction wave of cystine to more negative potentials but the displaced waves do not rise as steeply as do the waves displaced by thymol. Camphor exerts a very peculiar effect on the reduction wave of cystine as is seen in Fig. 2 which depicts the effects of varying concentrations of camphor on the c. v. curve of 0.001 *M* cystine in 0.1 *N* hydrochloric acid. It is seen that the displaced waves rise more steeply the greater the concentration of camphor and also that in the solution which was saturated with camphor (curve 4) the wave is displaced by almost one volt.

The diffusion current of cystine at *pH* 1.0 may be determined readily if the maximum is eliminated with thymol. It is seen from Table I that the true diffusion current, i_d , is directly proportional to the concentration of cystine in the range of concentrations investigated. The diffusion currents were determined at -0.7 volt (*vs.* S. C. E.).

From these values of the diffusion current one can calculate the diffusion coefficient of cystine

TABLE I
PROPORTIONALITY BETWEEN i_d AND CYSTINE
CONCENTRATION

Concn. of RSSR in millimoles per liter	i_d app.	i res.	i_d	i_d/C
0.5	3.62	0.16	3.46	6.92
1.0	7.14	.16	6.98	6.98
1.5	10.56	.16	10.40	6.93

in 0.1 *N* hydrochloric acid by means of the Ilkovic⁶ equation, $i_d = 605nD^{1/2}Cm^{2/3}t^{1/6}$, in which n is the number of electrons involved and is equal to 2 in this case, C the concentration of cystine in millimols per liter, m the number of mg. of mercury flowing from the capillary per second and t the time in seconds required for the formation of one drop of mercury. The value of $m^{2/3}t^{1/6}$ for the capillary used was 2.483. Substituting the known values into the Ilkovic equation and solving for D we find that the diffusion coefficient of cystine in 0.1 *N* hydrochloric acid at 25° is 5.3×10^{-5} cm.²/sec.^{6a}

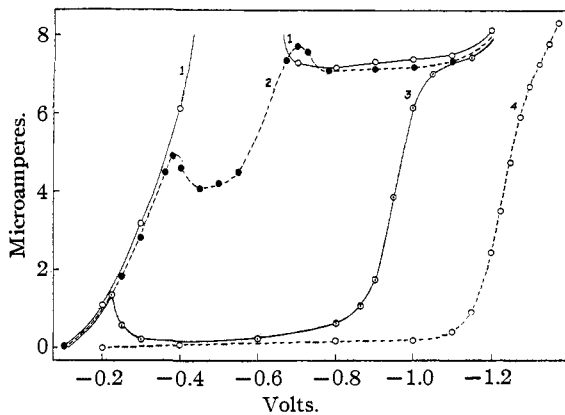


Fig. 2.—Effect of camphor on the curve of 0.001 *M* cystine in 0.1 *N* hydrochloric acid: (1) no camphor (maximum reached at 20.35 microamperes); (2) 3.5×10^{-4} *M*; (3) 10^{-3} *M*; (4) saturated.

Current-voltage Curves Obtained at Other Values of the *pH*.—In 0.98 *N* hydrochloric acid cystine gave a c. v. curve which almost coincided with the curve in 0.1 *N* hydrochloric acid. However, the diffusion current in the more acid medium was poorly defined and appeared to be a few per cent. smaller than in 0.1 *N* hydrochloric acid. This difference may be attributed to the fact that the cystine cation has a smaller diffusion

(6) D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934).

(6a) Due to an arithmetical error the value of D cysteine reported in a previous paper [THIS JOURNAL, **62**, 3061 (1940)] was given as 3.1×10^{-5} instead of 7.0×10^{-5} cm.² sec.⁻¹ at 25° in 0.1 *N* perchloric acid.

coefficient than the neutral molecule. At *pH* 2.0 (Clark and Lubs buffer) there also occurred a maximum on the c. v. curve of cystine which could be suppressed by capillary active substances. The curve at this *pH* occurred at a more negative potential than did the curve in 0.1 *N* hydrochloric acid.

Between *pH* 3 and 7 cystine is very slightly soluble and saturated solutions at 25° have a concentration from 4 to 7×10^{-4} *M*. Since the c. v. curve of cystine shows such an extremely small slope at small concentrations it was felt desirable to use saturated solutions for the study in this *pH* range. Above a *pH* of 2 the maximum on the reduction curve of cystine no longer appeared and hence it was unnecessary to add thymol for suppression of maxima. However, there did appear two-step waves as may be seen from the c. v. curves of saturated solutions of cystine at *pH* values between 4.73 and 9.2 as shown in Fig. 3.

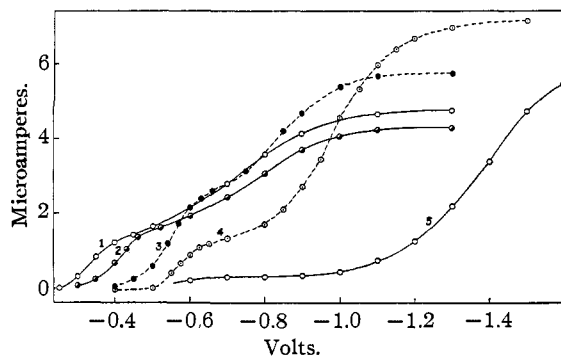


Fig. 3.—Effect of *pH* on cystine wave: (1) saturated cystine at *pH* 4.73 (acetate buffer); (2) saturated at *pH* 6.0 (phosphate buffer); (3) saturated at *pH* 8.0 (phosphate buffer); (4) 0.001 *M* at *pH* 9.2 (borax buffer); (5) 0.001 *M* in 0.1 *N* sodium hydroxide.

It is seen that the latter step of these waves has a very small slope but that the first step has much the appearance of a reversible reduction wave. It is readily seen that the potential at which the first step occurs depends upon the *pH* and is shifted to more negative values with increasing *pH*. This shift of potential was found to be approximately 56 millivolts per *pH* unit. Between *pH* 4.73 and 8.0 the relative height of the first step with respect to the total wave steadily increased. At a *pH* of 9.2 the relative height of the first step began to decrease. In 0.1 *N* sodium hydroxide (curve 5) the first step had completely disappeared and the c. v. curve had a slope corresponding to a typical irreversible reduction.

Cystine Reduction Waves after Saturation with Camphor.—We have already seen that when a solution of cystine at pH 1.0 is saturated with camphor the c. v. curve is shifted to more negative potentials by almost one volt. In addition the curve rises more steeply than in the absence of camphor. Camphor exerts a similar effect on the c. v. curves of cystine at other values of the pH . From Fig. 4 it is apparent that saturation with camphor shifts the curves of cystine at pH 1 and 2 to exactly the same negative potentials. At pH 3 camphor shifts the cystine wave to more negative potentials than at pH 1 and 2 and, furthermore, the curve has not as steep a slope as have the curves at pH 1 and 2. At pH values between 4 and 9.2 camphor shifts the beginning of all the waves to about -1.35 volts which is seen to be even more negative than the potential to which the curve at pH 3 is shifted. Figure 4 further shows that the first portion of the curve of cystine in $0.1 N$ sodium hydroxide is also shifted to -1.35 volts but that the latter portion of the wave follows its normal course (compare with Fig. 3).

Discussion

1. The marked shift of the reduction wave of cystine to more negative potentials by the addition of capillary active substances such as thymol, camphor or gelatin has never been noticed before in other cases in the polarographic literature. The effect indicates that the cystine must be oriented (adsorbed) in a favorable position at the surface of the dropping electrode before it can be reduced. Apparently, the capillary active substances prevent or counteract orientation (adsorption) of the cystine at the surface of the electrode and thus displace the curve to more negative potentials. The effect of camphor is particularly striking (see Fig. 2). When the concentration of camphor is small the initial portion of the reduction wave coincides with the wave (showing the pronounced maximum) obtained in the absence of camphor. Apparently, the camphor at these small concentrations is unable to prevent the orientation of cystine completely. With increasing negative potentials the adsorption of camphor is apparently favored and, depending on the camphor concentration, the current suddenly decreases and the remainder of the wave is displaced to more negative potentials. A quantitative interpretation of the phenomenon is not possible at present; we do not know the

relative adsorbabilities of camphor and cystine at various potentials of the mercury drop, nor do we know the speeds of adsorption and orientation which undoubtedly also play a part. The effect of camphor at various pH values is given in Fig. 4.

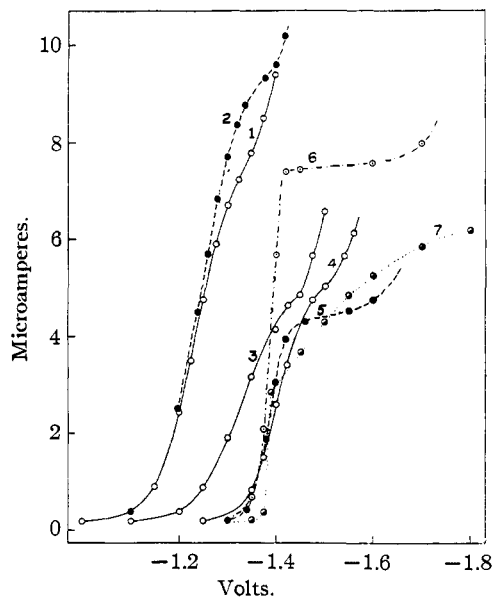


Fig. 4.—Effect of saturation with camphor on cystine waves at various pH values: (1) $0.001 M$ cystine in $0.1 N$ hydrochloric acid; (2) saturated at pH 2.0 (Clark and Lubs buffer); (3) saturated at pH 3.0 (acetate buffer); (4) saturated at pH 4.0 (acetate buffer); (5) saturated at pH 6.0 (phosphate buffer); (6) $0.001 M$ at pH 9.2 (borax buffer); (7) $0.001 M$ in $0.1 N$ sodium hydroxide.

The behavior of camphor alone at the dropping mercury electrode has been studied by Tachi.⁷ Lack of space does not permit discussion of the various small waves found by Tachi. Evidence obtained by us shows that these small "waves" do not correspond to a reduction of camphor but must be attributed to electrocapillary phenomena. Camphor is strongly capillary active at the water-mercury interface. This is evident from the electrocapillary curves given in Fig. 5 where the drop time is plotted against the potential in a medium of $0.1 N$ hydrochloric acid and in the same medium saturated with camphor. It is seen that the electrocapillary zero is shifted to more positive potentials by the camphor. The adsorption of camphor decreases with increasing negative potentials, and the two electrocapillary curves coincide at a potential of about -1.28 volts (*vs.* S. C. E.). Hence at this potential the cam-

(7) I. Tachi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **42**, Chem. Series No. 22, 42 (1938).

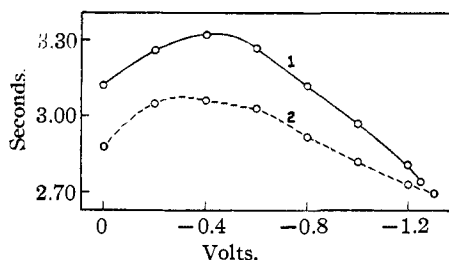


Fig. 5.—Effect of camphor on electrocapillary curve in 0.1 *N* hydrochloric acid: (1) no camphor; (2) saturated with camphor.

phor is completely desorbed and can no longer interfere with the reduction of cystine at the dropping electrode. This is the reason that the reduction of cystine in solutions with a *pH* of 1 to 2 which are saturated with camphor is shifted to a potential of -1.2 volts. At *pH* values greater than 4 we found that the electrocapillary curves in the absence and presence of camphor coincided at about -1.4 volts. Again it was found that the cystine waves were displaced to about this potential at *pH* values greater than 4 when the solutions were saturated with camphor. Naturally then, in solutions saturated with camphor the *pH* effect upon the reduction of cystine hardly occurs at all. The reduction cannot occur until a potential is reached at which all of the camphor is desorbed while the "normal reduction wave" of cystine would start at much more positive potentials. The above conclusions are also substantiated by the following experiment. In Fig. 6 is given the residual current in a borax buffer at *pH* 9.2 and also in the same buffer saturated with camphor. A small wave starting at about -1.35

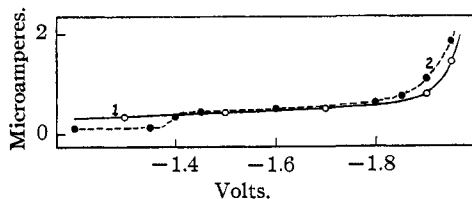


Fig. 6.—Effect of camphor on residual current at *pH* 9.2 (borax): (1) no camphor; (2) saturated with camphor.

volts is clearly noticeable in the buffer saturated with camphor. In agreement with Tachi we conclude that this wave is not due to a reduction of camphor but to the desorption of camphor from the surface of the electrode. The normal residual current in the absence of camphor is a charging current,⁸ its value depending upon the capacity

(8) I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

of the double layer. This capacity is quite different in the presence of adsorbed camphor than in its absence from the surface as is seen from Fig. 6. At potentials between -1.35 and -1.45 volts the camphor is being desorbed and the residual current becomes equal to that in the absence of camphor at potentials more negative than -1.45 volts. The peculiar shape of the wave obtained from a cystine solution in 0.1 *N* sodium hydroxide which is saturated with camphor is now easily explained. Curve 1 of Fig. 7 gives the reduction of cystine at *pH* 13 in the absence of camphor while curve 2 gives the reduction in the same solution which is saturated with camphor. As is seen the beginning of the wave is shifted to more negative potentials in the presence of camphor. The reduction does not start until the potential is -1.35 volts. Between -1.35 and -1.45 volts the camphor is being desorbed and the c. v. curve has a very steep slope. At potentials more negative than -1.45 volts the camphor is completely desorbed and curve 2 is seen to practically coincide with curve 1 from there on.

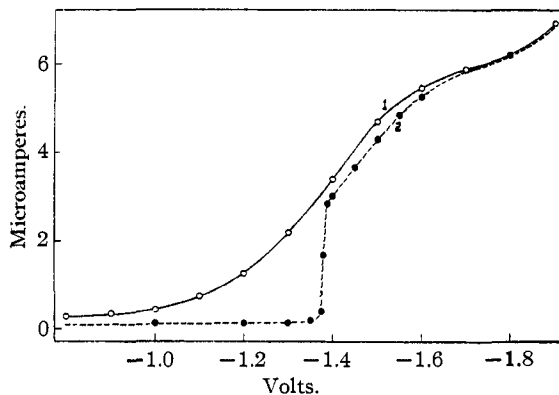


Fig. 7.—Effect of camphor on curve of cystine in 0.1 *N* sodium hydroxide: (1) 0.001 *M* cystine; (2) same saturated with camphor.

2. Since cystine at a mercury electrode is reduced to cysteine,⁹ RSH, the reaction occurring at the dropping electrode may be represented by the equation $RSSR + 2H^+ + 2e \rightarrow 2RSH$. In the experimental part we have seen that most waves of cystine are very drawn out and that their appearance does not correspond to that of a reversible reaction involving the transfer of two electrons. Only the waves at a *pH* of the order of 1 in which the maxima were eliminated by a minimum amount of thymol had a more normal

(9) J. C. Ghosh, S. N. Raychadhuri and S. C. Ganguli, *J. Indian Chem. Soc.*, **9**, 43 (1932).

appearance. If at this pH the electrode at each potential on the wave were in equilibrium with the surrounding solution and the electrode reaction were reversible it can be derived¹⁰ that

$$\pi = C - 0.059 pH + 0.0295 \log (i_d - i)/i^2 \quad (1)$$

in which π is the potential at each point on the wave, C is a constant, i_d the diffusion current and i the current at the potential π . Thus when π is plotted against $\log (i_d - i)/i^2$ a straight line with a slope of 0.0295 should be obtained. The analysis of the wave obtained at a pH of 1 in the presence of $2.4 \times 10^{-5} M$ thymol yielded a straight line as shown in Fig. 8. However, the slope was

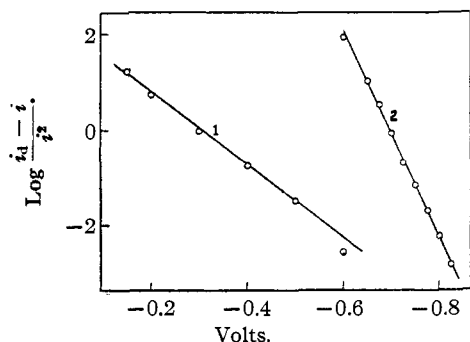


Fig. 8.—Analyses of cystine waves in 0.1 N hydrochloric acid in the presence of thymol: (1) 0.001 M cystine, $2.4 \times 10^{-5} M$ thymol; (2) 0.001 M cystine, $4.8 \times 10^{-4} M$ thymol.

found to be 0.132 instead of the theoretical value of 0.0295. With increasing thymol concentration the wave was displaced to more negative potentials and the slope of the log plot line became close to the theoretical. For example, in the presence of $4.8 \times 10^{-4} M$ thymol a slope of 0.046 was found. Similar relations were found to hold for waves obtained in the presence of camphor. Again a straight line was found with a slope of 0.048 for the reduction of cystine at pH 1 in the presence of $2 \times 10^{-3} M$ camphor. Also a straight line was found in the analysis of the cystine wave at pH 2 in the presence of 0.01% of gelatin but this line had a slope of 0.150. From the above it is evident that even in the most favorable cases none of the waves gave an analysis which corresponded to a thermodynamically reversible reaction. Apparently, the electrode is polarized at potentials on the wave where the cystine is being reduced; at present it is not possible to give the exact cause of this polarization. Undoubtedly, adsorption of cystine on the surface of the mercury drop and the speed of orientation of the molecule are factors to be considered.

(10) For derivations see reference (2).

Since the plot of π against $\log (i_d - i)/i^2$ yields a straight line it can be inferred that the half-wave potential, that is, the potential at which $i = i_d/2$, should shift slightly to more negative potentials with increasing cystine concentration. This relationship was found to hold.

3. The two-step waves found at pH values between 3 and 9.2 need explanation. In a subsequent paper experimental evidence will be given which shows that the first step of the waves does not correspond to a true reduction of cystine. Although the following reaction occurs in the reduction of cystine at the dropping electrode, $RSSR + 2H^+ + 2e \rightarrow 2RSH$, the reverse reaction does not occur anodically with cystine. In a previous paper² we have seen that the anodic wave of cystine is due to the reaction $RSH + Hg \rightleftharpoons HgSR + H^+ + e$. Figure 9 gives the observed reduction wave of cystine and the anodic wave of cystine at a pH of 6. The dotted line, 1, is an extrapolation of the second step of the cystine wave and represents the hypothetical "true reduction wave."

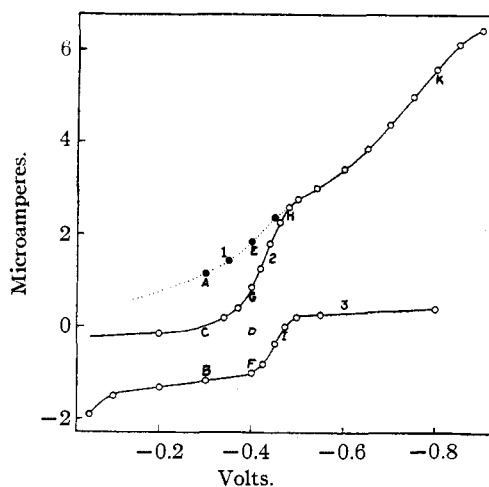


Fig. 9.—Hypothetical reduction curve of cystine at pH 6.0: (1) hypothetical reduction curve; (2) experimental reduction curve of 0.001 M cystine; (3) anodic wave of 0.002 cysteine.

Let us first consider point C on the experimental reduction wave. At this point the current is zero and the potential corresponds to the potential of the cystine solution at the dropping electrode. This is a typical "mixed potential" in the sense of Kolthoff and Miller.¹¹ Actually a reduction of cystine occurs at this potential, the cathodic current being equal to CA. However, the cystine formed reacts immediately with mercury at this

(11) I. M. Kolthoff and C. S. Miller, *THIS JOURNAL*, **62**, 2171 (1940).

potential to yield HgSR and the anodic current CB is equal to CA. Similarly, at a potential D the actual current DG is equal to the difference between the hypothetical cathodic current DE and the anodic current DF. At the potential I the cysteine no longer yields an anodic current and the experimental current IH now corresponds to the true reduction current of cystine. The same, of course, is true at potentials more negative than I, and the experimental curve HK is also the true reduction wave. In conclusion it may be mentioned that potentials of the cystine-cysteine system measured with the dropping mercury electrode do not correspond to the thermodynamically reversible potentials of the system $\text{RSSR} + 2\text{H}^+ + 2e \rightleftharpoons 2\text{RSH}$ but represent typical "mixed potentials."

Summary

1. Cystine may be determined polarographically at a *pH* of 1 using thymol to suppress the maximum. The diffusion current was found to be proportional to the concentration.

2. The diffusion coefficient of cystine was calculated to be 5.3×10^{-6} sq. cm./sec. in 0.1 *N* hydrochloric acid at 25°.

3. An analysis of the current-voltage curves shows that the reduction of cystine at the dropping electrode does not occur reversibly according to the reaction $\text{RSSR} + 2\text{H}^+ + 2e \rightleftharpoons 2\text{RSH}$, although the effect of *pH* upon the potential is given approximately by this equation.

4. Capillary active substances such as thymol, camphor, gelatin and methylene blue markedly shift the reduction curves of cystine to more negative potentials. It is proposed that this is caused by their inhibiting the orientation or adsorption of cystine at the surface of the mercury drop.

5. The first step in the waves obtained with cystine in buffer solutions with a *pH* between 3 and 9.2 is explained by the fact that the cystine formed by reduction reacts anodically with mercury with the formation of mercurous cysteinate. The first step of the wave does not correspond to the true reduction wave of cystine, while the second step does represent the true reduction wave. The potential of cystine-cysteine solutions at the dropping electrode is a typical "mixed potential."

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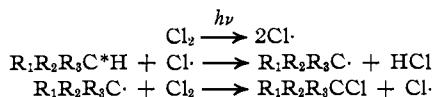
RECEIVED NOVEMBER 7, 1940

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Reactions of Atoms and Free Radicals in Solution. II. The Non-Isomerization of Free Alkyl Radicals in Solution

By M. S. KHARASCH, STEPHEN S. KANE¹ AND HERBERT C. BROWN

In the first paper of this series,² the photochemical chlorination and the peroxide-catalyzed chlorination of primary active amyl chloride were studied. The fact that the substitution of a chlorine atom for a hydrogen atom on the asymmetric carbon atom results in an inactive product was interpreted as support for the hypothesis that the reaction proceeds through a chain mechanism involving the momentary existence of a free alkyl radical.

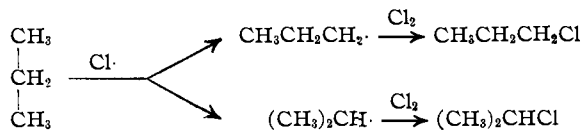


In drawing this conclusion from the experimental results, the tacit assumption was made

(1) This paper is part of a dissertation submitted by Stephen S. Kane to the Faculty of the Division of the Physical Sciences of the University of Chicago, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Brown, Kharasch and Chao, *THIS JOURNAL*, **62**, 3435 (1940).

that the substituent enters the molecule in the position left vacant by the removal of the hydrogen atom; in other words, that no rearrangement of the free radical occurs in the process of formation of the product. On the basis of this assumption the proportions of *n*-propyl and isopropyl chlorides in the chlorination product of propane should be the same as the proportions of the corresponding free radicals first formed.



Recently, however, Glazebrook and Pearson³ have reported that free radicals may undergo an isomerization with the result that the structure of the final product is not necessarily determined by

(3) Glazebrook and Pearson, *J. Chem. Soc.*, 1777 (1936).