Oxidation-Reduction Reactions in Stirred Liquid-Liquid Systems

G. A. MANSOORI and A. J. MADDEN
University of Minnesota, Minneapolis, Minnesota

Oxidation-reduction rates have been determined in stirred liquid-liquid systems wherein tetravalent cerium ions in a continuous aqueous phase were reduced by tetrachlorohydroquinone contained in dispersed organic droplets. Kinetic data obtained (using low volume fractions (<0.06) of dispersed organic phase) indicate that the rate of reduction of ceric cerium is proportional to the extent of the interfacial area of the stirred liquid-liquid system. Two possible rate-limiting mechanisms are discussed to explain the observed kinetic behavior.

This liquid-liquid electron exchange system might find potential use as a chemical tool for measuring changes in interfacial area as influenced by various mixing parameters.

An extremely interesting special class among heterogeneous reaction systems is that of liquid-liquid electron exchange. Scibona, Danesi, and Orlandini (*13*) recently pointed out the possible application of this type of system in the processing of aqueous solutions. Thus, for example, aqueous solutions of multivalent metallic ions can be reduced or oxidized by their contact with an immiscible organic phase containing, appropriately, an organic-soluble reductant or oxidant. The result is a change in the valence state of a species in the aqueous phase without introduction of extraneous components, except for the addition or removal of a proton. For this to be effectively achieved the reactants (and their oxidation or reduction products) must be substantially insoluble in the opposite phase.

As these authors pointed out, the same result can be accomplished by using solid electron-exchange polymers (*5*) but the use of a liquid-liquid system offers the possibility of faster oxidation-reduction rates. Their proposal, in essence, suggests an analogous development in the general area of heterogeneous electron exchange reactions to that which has occurred in the field of ion exchange. In that area liquid ion exchange (*9*) has assumed an important processing role in recent years, particularly in nuclear technology for recovering uranium and related values from ore-leach liquors (*4, 6*). Since the technique for conducting liquid ion exchange operations is identical to that employed for general solvent extraction, the same advantages would accrue to liquid electron exchange operations. In particular, the ease of adaptation to continuous, countercurrent contacting would be a noteworthy operational advantage.

The study of Scibona, Danesi, and Orlandini (*13*) was the first to present any kinetic information on a system of this kind. Such data were restricted to reaction rates for the reduction of ferric ions [Fe(III)], contained in aqueous 1N perchloric acid by tetrachlorohydroquinone (TCH), present as a solute in an immiscible organic phase (90% xylene, 10% nonanol). The two phases were mixed in a mechanical shaker at constant speed and temperature. No information was given, however, as to how the reaction rates might be affected by changes in the degree of agitation, the relative volumes of the two phases or the temperature.

In this study rates of reduction of tetravalent cerium ions [Ce(IV)] by tetrachlorohydroquinone (TCH) in stirred liquid-liquid systems were investigated quite extensively. The aqueous phase was the continuous phase, contained the Ce(IV)* oxidant ions and was in all cases made 1N with respect to sulfuric acid. The immiscible organic dispersed phase (an equivolume mixture of carbon tetrachloride and 2-octanone) served as the solvent for the solid reductant, TCH. Dispersion was accomplished by stirring the two-phase system in a baffled beaker with a flat-blade, turbine impeller rotating at a constant speed. The influence of several variables on the kinetics of reduction of ceric ions [Ce(IV)] to cerous ions [Ce(III)] was considered. Among these were the concentrations of Ce(IV) and TCH in their respective phases, the volume of the dispersed organic phase, the rotational speed of the stirrer and the temperature.

An interesting deduction of the present work is that the rate of reduction of Ce(IV) by TCH appears to be directly proportional to the interfacial area of the stirred two-phase

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G. A. Mansoori is presently at P.O. Box 2162, Norman, Oklahoma.

* Throughout this paper ceric cerium will be identified as Ce(IV). Hardwick and Robertson (*7*) indicate that in $1NH_2SO_4$ the predominant ionic form involving ceric cerium is the sulfato-ceric anionic complex, $Ce(SO_4)_3^{--}$.

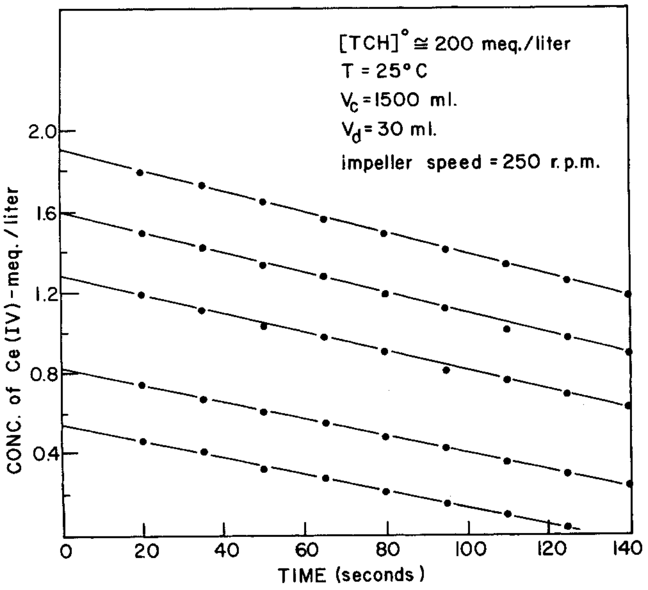


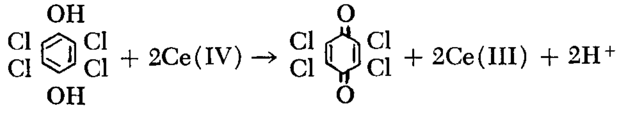
Fig. 1. The rate of reduction of Ce(IV) is independent of the Ce(IV) concentration in the aqueous phase.

system. Hence, this liquid-liquid reaction system might find potential use as a chemical tool for measuring changes in interfacial area as influenced by changes in various mixing parameters.

The rates of reduction of Ce(IV) were also found to be independent of the Ce(IV) concentration in the aqueous phase. This is in sharp contrast to the observations on Fe(III) reduction by Scibona, et al. who reported the rate to be directly proportional to the Fe(III) concentration.

THE TWO-PHASE REACTION SYSTEM

The overall reaction which occurred in the system investigated is given by the following equation:



(TCH) tetrachlorohydroquinone (TCQ) tetrachloroquinone

The two-phase system was contained in a 2-liter glass beaker, fitted with four glass bafflles (9/16 in. wide), symmetrically arranged. The assembly was immersed in a constant temperature water bath for temperature control. The continuous aqueous phase (1N sulfuric acid) was of the same volume (1,500 ml.) in all experiments and the initial ceric ion content was varied as desired from 0.5 to 2.0 mequiv./liter. The dispersed organic phase (equivolume mixture of carbon tetrachloride and 2-octanone) varied in volume from 15 to 90 ml. and the TCH content was investigated over the range 50 to 400 mequiv./liter. It is to be noted that the volume fraction of the dispersed organic phase was low, ranging from 0.01 to 0.056.

Stirring of the two-phase system was accomplished with a 3 inch diameter, stainless-steel, 6-blade turbine impeller driven by a constant speed motor through a gear train. By interchanging gears constant impeller speeds of 150, 175, 200, 250, or 300 rev./min. could be obtained. In all experiments the impeller was positioned centrally in the beaker with a 5 mm. clearance between the bottom of the beaker and the impeller blades.

To follow the progress of the oxidation-reduction reaction in the stirred system the ceric ion content of the aqueous phase was monitored as a function of time. This required periodic sampling of the continuous phase, generally at 15 sec. intervals, by withdrawing small samples through a sintered-glass sparger tube, which rejected the organic phase droplets and allowed clear aqueous phase samples to be collected. These samples were analyzed spectrophotometrically to determine the Ce(IV) content using a Beckman DU Spectrophotometer (*12*).

In conducting a typical experiment the more dense (density ≅ 1.2 g./ml.) organic phase (15 to 90 ml.) was added to 1,500 ml. of aqueous 1N sulfuric acid already at temperature equilibrium in the thermostatted beaker. The constant speed stirrer was then started and the organic phase, initially at the bottom of the beaker, was dispersed throughout the aqueous phase in the form of small droplets. After 5 min. of stirring to achieve an equilibrium drop size distribution, the Ce(IV) content of the aqueous phase was adjusted by the addition of a small volume of concentrated ceric sulfate solution. (It was found that stirring times of 5 min. or longer prior to the addition of ceric ions gave similar reaction rates. Hence, for uniformity of procedure a 5 min. predispersion time was used in all experiments.) The progress of the reaction was then followed by removing clear samples of the aqueous phase periodically to determine the Ce(IV) content. Visual evidence of the progress of the reaction was the fading of the characteristic yellow color of ceric ions as these were reduced to the colorless cerous form.

The chemicals used were tetrachlorohydroquinone, ceric sulfate, 2-octanone, and carbon tetrachloride. All were used as received except for the 2-octanone which was redistilled. The solubility characteristics of reactants and products were as follows: TCH (solubility in organic phase, 500 mequiv./liter at 25°C.), TCQ (solubility in organic phase, 30 mequiv./liter for TCQ at 25°C.), TCH and TCQ, both only sparingly soluble in the aqueous phase, Ce(IV) ions and Ce(III) ions—water soluble, essentially insoluble in the organic phase.

EXPERIMENTAL RESULTS

The effect of a number of variables on the rate of re-

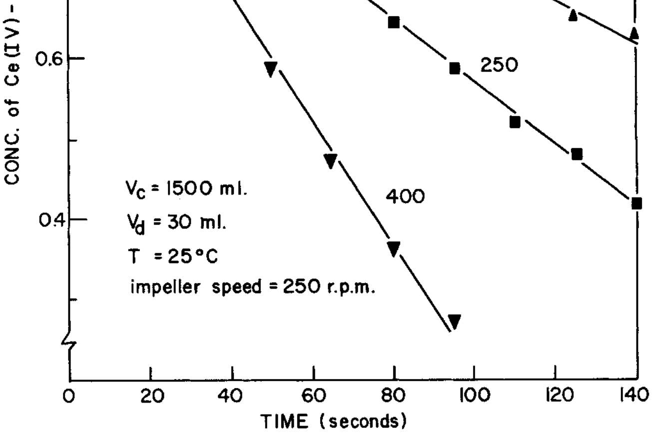


Fig. 2. Typical data showing that the rate of Ce(IV) reduction is markedly affected by the TCH concentration in the organic phase. [(TCH)° indicates initial concentration].

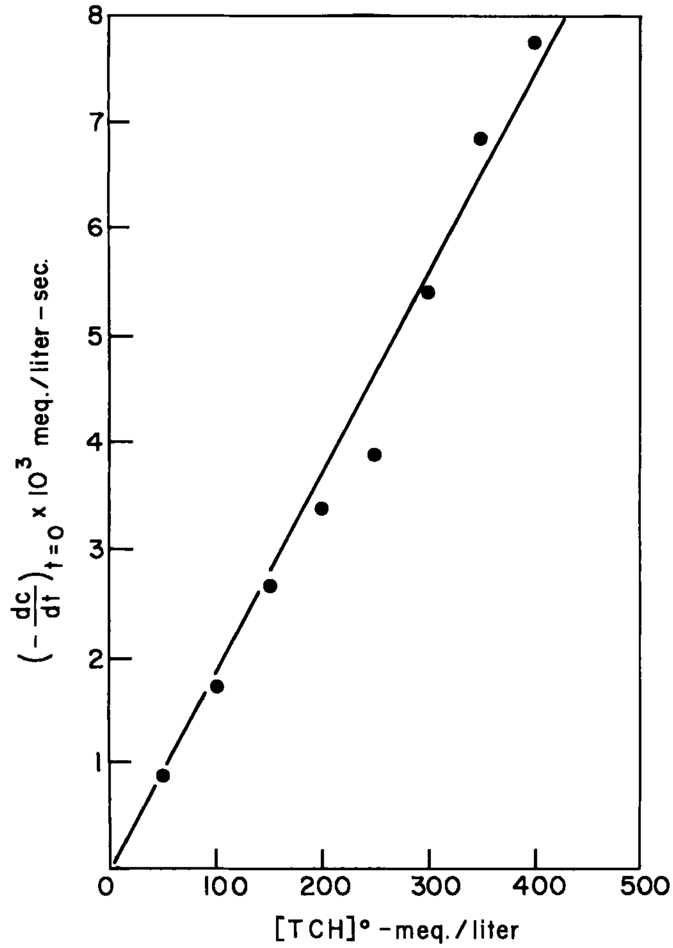


Fig. 3. Analysis of data for various TCH concentrations (some shown in Figure 2.) indicates that the rate of reduction of Ce(IV) is directly proportional to TCH concentration.

duction of Ce(IV) was investigated. In each series of experiments only a single parameter was varied. The results, shown graphically in Figures 1 to 6, may be summarized for the range of variables considered as follows. The rate of reduction of Ce(IV) in the continuous aqueous phase is independent of the Ce(IV) concentration (Figure 1), directly proportional to the TCH concentration in the dispersed organic phase (Figures 2 and 3) and is directly proportional to the dispersed phase volume (Figure 4).

Furthermore, the rate increases with an increase in stirring speed (Figure 5) and as Figure 6 indicates, the rate is proportional to (impeller speed)$^{\sim 1.4}$. A fairly strong temperature dependence is also shown in Figure 6 where the rate of reduction is seen to increase approximately 70% for a 10°C. temperature rise (15 to 25°C.).

INTERPRETATION OF RESULTS

Abramzon and Kogan (2) have generalized that whenever a liquid-liquid reaction involves an ionic and a nonionic reactant the reaction proceeds almost exclusively in the aqueous phase. Whether the reaction proceeds throughout the whole of the aqueous phase or is confined to a reaction zone close to the interface depends upon the relative rates of the chemical reaction and various physical transport processes which may be involved.

The observation that the rate of reduction of Ce(IV) is directly proportional to the dispersed phase volume and to (impeller speed)$^{\sim 1.4}$ is strongly suggestive that the rate is directly proportional to the interfacial area. Studies of interfacial areas in stirred liquid-liquid systems have shown that, for dilute dispersions, interfacial area is proportional to dispersed phase volume and to (impeller speed)^x. Values of x found in different studies range from 0.75 to 1.9 (*11, 17*). These findings give reasonable support to the interpretation offered for the observations of the present study. This suggests that this liquid-liquid reaction system might find potential use as a chemical tool for measuring interfacial area changes as influenced by alteration of various mixing parameters.

To explain further the observed kinetic behavior of the TCH-Ce(IV) reaction system any proposed mechanism must be consistent with the additional observations that the rate of reduction of Ce(IV) is directly proportional to the TCH concentration in the dispersed organic phase and is independent of the Ce(IV) concentration in the aqueous phase. Following the argument of Abramzon and Kogan (2), it will be assumed that the chemical reaction occurs in the aqueous phase. This requires the transfer of TCH across the interface from the organic phase to the continuous aqueous phase where chemical reaction with Ce(IV) takes place. Two possible rate-limiting mechanisms will be considered.

The experimental observations would be consistent with the theory of extraction accompanied by a rapid first-order chemical reaction (*1*). When applied to the present system and invoking the usual assumption that the solute (TCH) is at physical partition equilibrium at the interface, the rate of reduction of Ce(IV) would be given by the following equation.

$$-V_c\frac{dc}{dt} = K_p[\text{TCH}]\ S\sqrt{Dk} = K'[\text{TCH}]S \qquad (1)$$

This equation predicts that the rate of reduction of Ce(IV) is independent of the aqueous Ce(IV) concentration and directly proportional to both the interfacial area and the TCH concentration of the dispersed organic phase. The proportionality constant, $K' = K_p\sqrt{Dk}$, is seen to depend only upon physico-chemical properties and is independent of system hydrodynamics.

Since no data could be found for the kinetics of the

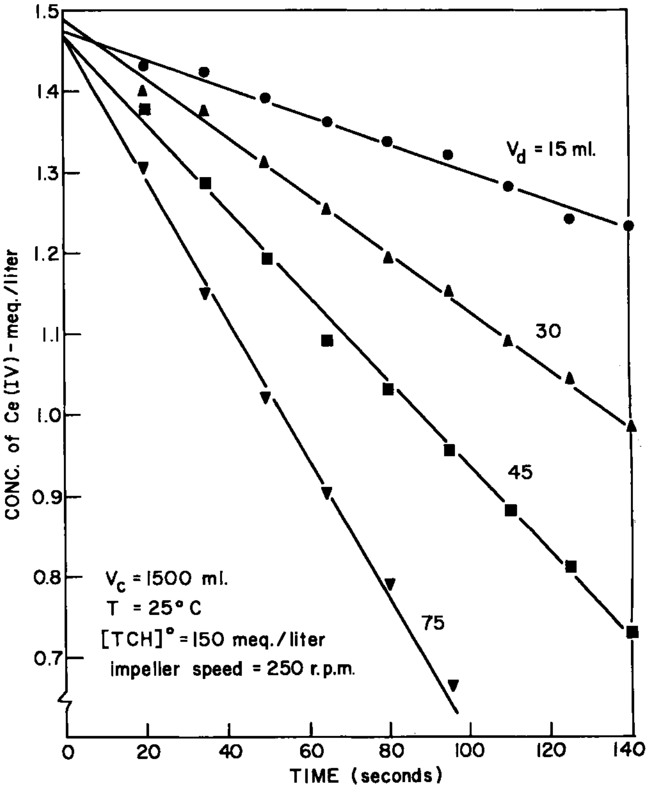


Fig. 4. Effect of dispersed phase volume on the rate of reduction of Ce(IV). Analysis shows rate to be directly proportional to dispersed phase volume.

TCH-Ce(IV) reaction in a homogeneous system, it is impossible to say that the kinetic behavior can be realistically described as being zero order in Ce(IV), a requirement needed for this equation to apply. Studies of homogeneous oxidation-reduction kinetics involving Ce(IV) and other organic hydroxy compounds [ethylene glycol (*8*) and pinacol (*10*)] indicate that the rate of reduction of Ce(IV) is first order with respect to both Ce(IV) and the organic compound in each case. Thus, one is left with the uncomfortable feeling that the agreement between observation and prediction via this mechanism may be fortuitous. This raises the question of a possible alternate rate-limiting process.

Could it be that the rate of the chemical reaction is very rapid compared with the rate of passage of TCH across the interface? If this is the case, the rate of reduction of Ce(IV) would be independent of the detailed kinetics of the chemical reaction and limited by the interfacial transfer rate of the TCH. Yamazaki and Piette (*18*) observed that the homogeneous reaction between Ce(IV) and hydroquinone (the parent reductant) is very rapid and this suggests that a similar situation might well be true for the Ce(IV)-TCH reaction. It is more diffcult to find closely-allied, suggestive evidence to support the notion that there may be a significant interfacial resistance to the transfer of TCH. However, Sinfelt and Drickamer (*15*) found such to be the case for the transfer of tagged sulfur across saturated liquid-liquid interfaces. Specific velocity constants for interfacial sulfur transfer from *n*-heptane to a number of other liquids were found to vary markedly, ranging from 5.29 × 10^{-4} cm./sec. (heptane → nitrobenzene) to 4.4 × 10^{-7} cm./sec. (heptane → formic acid). Tung and Drickamer (*16*) pointed out that resistance to motion in the interface must be important in many, if not most, partially miscible systems. They cautioned further that it is not safe to assume equilibrium at the interface as is done in many chemical engineering calculations. This standard assumption, it will be recalled, was involved in establishing Equation (1).

If the interfacial rate of transfer of TCH is rate-limiting, the maximum flux of solute across unit area of interface would be proportional to the TCH concentration in the organic phase. This assumes the validity of the phenomenological theory for diffusion across an interface advanced by Scott, Tung, and Drickamer (*14*). Thus, the rate of Ce(IV) reduction would be given by the following equation

$$-V_c \frac{dc}{dt} = k_{ow}[\mathrm{TCH}]S \qquad (2)$$

This equation is of similar form to Equation (1) with the proportionality constant k_{ow}, like K', being independent of system hydrodynamics. There is an important distinction, however, in that k_{ow} is independent of the chemical reaction and, thus, the rate of reduction is independent of the detailed kinetics of the chemical reaction. Hence, if another oxidant were studied in the aqueous phase in place of Ce(IV) (for example, dichromate ion) and if it reduced rapidly in relationship to the interfacial transfer rate of TCH, it would be expected to reduce at the same limiting rate (in equivalents/time).

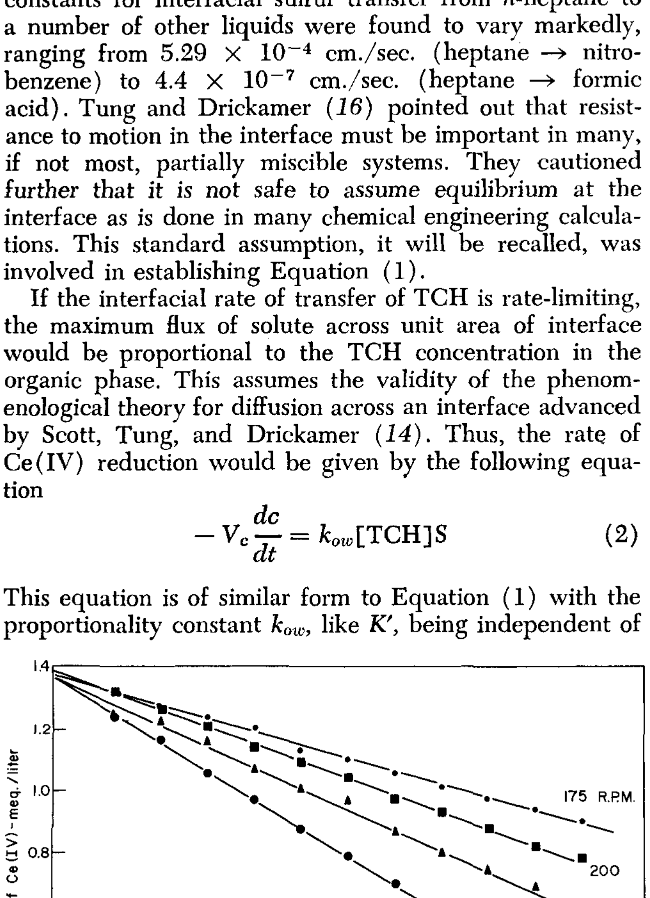


Fig. 5. The rate of reduction of Ce(IV) increases with increase in impeller stirring speed.

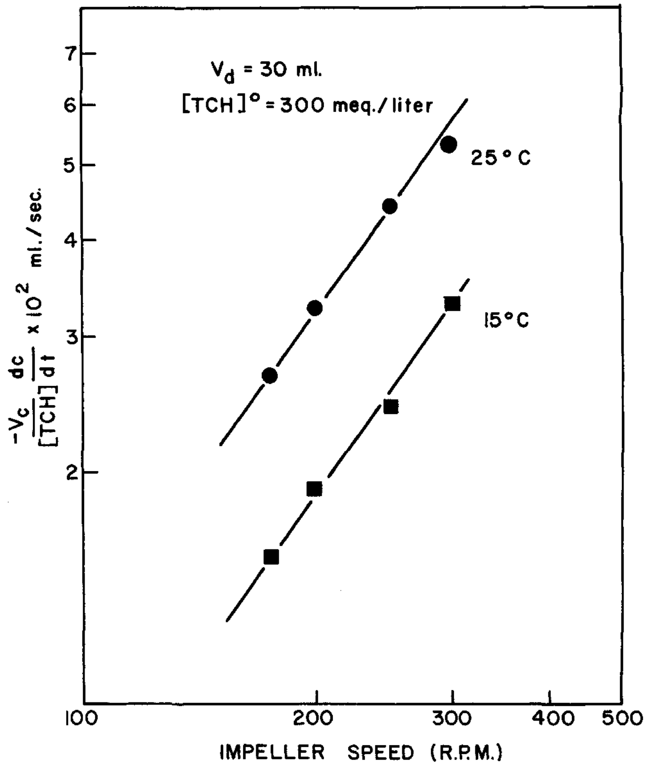


Fig. 6. The rate of reduction of Ce(IV) (proportional to the ordinate) varies with (stirring speed)~$^{1.4}$ and increases approximately 70% for a 10°C. temperature rise.

It is clear from the foregoing discussion that critical gaps in available information rule out a clear cut choice of mechanism to explain the present results. The reduction rates of other oxidants should be considered, since the available data are restricted to Ce(IV). Such additional data would be informative per se and, hopefully, might assist in clarifying the mechanistic picture.

OTHER EXPERIMENTAL RESULTS

One other experiment was conducted in support of the argument that the reaction rate is directly proportional to the interfacial area. This was done by carrying out the reaction under conditions where the interfacial area was known approximately. The organic phase containing TCH was placed at the bottom of a 500 ml. beaker. The aqueous phase was placed on top of it and only the aqueous phase was gently stirred so that a relatively quiescent interface (estimated at 42 sq.cm.) existed between the phases. The rate of reduction of Ce(IV) was monitored and by using Equation (1) or (2), the proportionality constant, K' or k_{ow}, was calculated to be about 5.21 × 10^{-6} cm./sec. at 35°C. Using this value and experimental rate data on a completely dispersed system (at 250 rev./min., 35°C.), the interfacial area of the stirred dispersion was calculated and found to be about 1.26 × 10^4 sq.cm. For the 30 ml. of dispersed phase used in this experiment, this area corresponded to a Sauter mean drop diameter of about 143 μ, which is in the proper range for this stirred system.

Throughout this study only Ce(IV) was studied as the oxidant, but a few experiments were carried out in stirred dispersed systems using another hydroquinone derivative as a reductant in place of TCH. This was 2,5 di-t-amyl hydroquinone. It was found that under otherwise comparable conditions the rates of reduction of Ce(IV) using this reductant were markedly lower (by a factor of 50). Clearly, the structure of the reductant has an enormous influence on the rate and should be considered in more detail in future work.

COMPARISON WITH THE TCH-Fe(III)

A complete comparison of the present results on the TCH-Ce(IV) system with those of Scibona, Danesi, and Orlandini (*13*) on the TCH-Fe(III) system is virtually impossible. A number of parameters were not investigated in their work and, also, the basic compositions of both the organic and the aqueous phases differed in the two studies. However, there are some notable differences that can be pointed out. They made the qualitative observation that Ce(IV) was reduced very rapidly by TCH when tried in their system and that, by contrast, the TCH-Fe(III) reaction was very slow. Furthermore, they found that the rate of reaction was proportional not only to the concentration of TCH in the organic phase but also to the concentration of Fe(III) in the aqueous phase as well. This latter finding differs from the observation of the present study that the rate is independent of the oxidant [Ce(IV)] concentration in the aqueous phase. They interpreted the observed rates of the TCH-Fe(III) system in terms of a second-order chemical reaction at the interface.

It is interesting to speculate on a rather different interpretation of their results. Assume that the chemical reaction also occurs in the aqueous phase in their system, but that the chemical reaction rate is slow relative to physical transport rates and is, thus, rate-controlling. Under these conditions the TCH concentration in the bulk aqueous phase would be maintained in partition equilibrium with the organic phase. Thus, the TCH concentration in the aqueous phase would be proportional to the TCH concentration in the organic phase. If the chemical reaction rate in the bulk aqueous phase is first-order with respect to both Fe(III) and TCH, then this interpretation is reconciled with their experimental results. Suggestive evidence that this may be the case is given by the observation of Baxendale and Hardy (*3*) that the kinetics of the homogeneous reaction involving Fe(III) and durohydroquinone (tetramethyl hydroquinone) is first-order with respect to both species.

If this interpretation is correct, the extent of the interfacial area would be of no consequence, since it assumes that the rate is limited by chemical reaction kinetics in the bulk aqueous phase. Thus, changes in stirring speed would not be expected to alter the rate of reaction. By contrast, their interpretation that it is an interfacial reaction that is rate-controlling should show a rate dependence on the agitation level. This question cannot be resolved, however, since no information was given as to the effect of agitation in their system. This analysis suggests, however, that in interpreting the kinetic behavior of liquid-liquid electron exchange systems consideration should be given to both the chemical kinetics and physical transport problems involved. The effect of operating variables can be quite different depending upon the rate-limiting process.

SUMMARY

Oxidation-reduction rates have been determined in stirred liquid-liquid systems wherein ceric ions in a continuous aqueous phase were reduced by tetrachlorohydroquinone contained in a dispersed organic phase. Kinetic data obtained (using low volume fractions (< 0.06) of dispersed organic phase) indicate that the reduction rate is proportional to the extent of the interfacial area. Assuming that reaction occurs in the aqueous phase, the observed rates of reduction of Ce(IV) may be limited by the interfacial transfer rate of TCH or accounted for by the theory of extraction accompanied by a rapid first-order reaction. A clear choice of mechanism cannot be made due to the lack of pertinent peripheral data.

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NOTATION

c = concentration of ceric cerium in the aqueous phase, mequiv./liter.
D = diffusivity of reductant (TCH) in reaction phase (aqueous), sq.cm./sec.
k = specific reaction velocity constant, sec.$^{-1}$
k_{ow} = velocity constant for interfacial reductant transfer from organic phase to aqueous phase, cm./sec.
K_p = equilibrium partition coefficient for reductant (TCH), concentration in aqueous phase/concentration in organic phase
N = impeller rotational speed, rev./min.
S = interfacial surface area, sq.cm.
t = time, sec.
[TCH] = concentration of tetrachlorohydroquinone in the organic phase, mequiv./liter
V_d = volume of dispersed phase, ml.
V_c = volume of continuous phase, ml.

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