

in stopping bleeding during surgery on the spleen, liver, and pancreas. One of its major medical contributions is that it has reduced, if not eliminated, the removal of injured spleens. Figure 2 is a photograph of AVITENE hemostat in a white fluffy physical form.

In 1974, after the commercial successes of both AVICEL microcrystalline cellulose and AVITENE microcrystalline collagen were well assured, I retired early. FMC/Alcon welcomed me to remain on the payroll in a state of "passive animation". They told me they did not expect to commercialize other inventions of mine until the high investment in AVITENE was substantially recovered and large profits began to build up.

Ergo, I started my own research institute and launched an extremely rewarding invention development and licensing career. The results have been uniquely rewarding. I have developed an environment of freedom, security, and mounting creativity never before experienced by me. My formula is consistent with the experimental facts of the two major case histories I have already described:

- (1) Each idea I conceive is reduced to practice in my own research institute.
- (2) U.S. Patents are filed just as soon as sufficient data to support a patent application are obtained. Unlike the situation that existed while I was employed by AVISCO/FMC for 33 years—when all of my patents were owned 100% by them—all of my patents received or pending since I retired are mine, owned wholly by me until I license them to appropriate licensees.
- (3) The exclusive world rights to the invention are

then offered by me—whenever at all possible—directly to the Chief Executive Officer of one or two companies who should have the highest motivation to champion the invention and bring it to the marketplace.

(4) My offers are overgenerous and hard to turn down: In return for *exclusive* and full ownership of the invention, all I ask is that I be retained as their consultant in support of the invention for a period of 2 years. This provision is to let me help them during the most difficult gestation period of a new invention.

(5) At the end of 2 years, they need not renew my consultancy agreement unless they wish to do so.

(6) A modest royalty must be paid only if and when the invention reaches commercial success—a term no licensee objects to because there is no obligation to pay royalties before and until *profits* are in hand.

Since my retirement, I have concluded many successful consulting—licensing agreements. These include agreements with Essilor (Paris); Capsugel (Basel); L'Oréal (Paris); Hormel; Smith, Kline, Beckman; Tandycrafts; and several other equally prestigious clients.

McGraw-Hill Book Company invited me to write a book about my career in pioneering the utility of polymer microcrystals.<sup>3</sup> This treatise tells it all for the first 20 years!

As a retired scientist, I have tasted the rewards of "Research For Profit" and the bottom line for The O. A. Battista Research Institute is in heavy black ink. Not surprisingly.

(3) Battista, O. A. "Microcrystal Polymer Science"; McGraw-Hill: New York, 1975.

## Kinetics and Mechanism of Metal Chelation Processes via Solvent Extraction Techniques

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Solvent extraction separation techniques provide simple and effective means for improvement of analytical methods by enhancement of sensitivity (by preconcentration) and selectivity (by interference removal).<sup>1</sup> Extraction techniques have proven of great service in metals analysis, particularly because a wide variety of extractants are available. In most instances the extent of extraction is independent of the total concentration of the metal, making it possible to describe optimal experimental conditions that are applicable both to extremes of "weightless" trace levels as well as macro levels that can be encountered in hydrometallurgical process technology.

Until about 40 years ago, kinetic aspects of solvent extraction were largely neglected. In most analytical extraction procedures, conditions favoring extraction

are usually sufficiently far from equilibrium so that vigorous shaking of the two phases serves to give essentially complete (>95%) extraction within several minutes. Some early work revealed qualitative dependence of extraction rates on such chemical variables as the nature of the organic solvent employed, pH, and extractant concentration.<sup>2-4</sup>

In 1962, Carl Honaker and I, intending originally to determine the equilibrium formation constant of the zinc chelate of diphenylthiocarbazone (dithizone) via solvent extraction, observed an unexpectedly slow attainment of extraction equilibrium.<sup>5</sup> The pink color in the aqueous phase, which indicated the formation of the positively charged 1:1 zinc chelate, persisted despite vigorous shaking for as long as 20 min. This observation launched a series of detailed systematic kinetic studies of extraction processes involving metal chelate forma-

Henry Freiser was born in New York City in 1920. He received his Ph.D. from Duke University and, after a year each at North Dakota State College and Mellon Institute of Industrial Research, became Associate Professor at the University of Pittsburgh. He moved to the University of Arizona in 1958 where he was for 10 years Head of the Chemistry Department and remains as Professor of Chemistry and Chairman of the Strategic Metals Recovery Research Facility today. Professor Freiser received from the American Chemical Society in 1978 the Fisher Award in Analytical Chemistry.

(1) Morrison, G. H.; Freiser, H. "Solvent Extraction in Analytical Chemistry"; Wiley: New York, 1957.

(2) Walkley, A. *Proc. Aust. Chem. Inst.* 1942, 9, 29.

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(5) Honaker, C. B., Freiser, H. *J. Phys. Chem.* 1962, 66, 127.

tion and dissociation. This work has led to a novel, simple, and effective technique for the study of the kinetics and mechanisms of inherently rapid reactions such as metal chelate formation, as well as to a clearer understanding of the intimate workings of solvent extraction processes, including an unequivocal evaluation of the role of the interface in extraction equilibria and kinetics.

Our study of the kinetic aspects of metal chelate extractions has addressed questions of both fundamental and practical interest. Some of the questions include the following: How are extraction rates affected by structural changes in the extractant? How large is the effect of ligand structure on reaction rates of metal chelate formation and dissociation? Does the nature of the rate-limiting step, i.e., the mechanism, change as the molecular weight and, therefore, the hydrophobicity of the extractant increases? When, if ever, does the liquid-liquid interface become significant?

Since its introduction in 1962, the method of determining the kinetics of inherently rapid reactions via solvent extraction has not attracted many users. Aside from Zangen who used this approach to determine the kinetics of the formation of mercury(II) bromide complexes,<sup>6</sup> Haraguchi, in the determination of the kinetics and mechanism of Ni complexes of 8-quinolinol,<sup>7</sup> 2-(2-thiazolylazo)-4 methylphenol, and 1-(2-thiazolylazo)-2-naphthol,<sup>8</sup> and two kinetic studies of organic reactions, rapid hydrolysis of esters<sup>9</sup> and carbonium ion reactions,<sup>10</sup> we remain essentially the sole practitioners of this method. For this reason, some attention to the methodology and its evolution would seem to be in order.

### The Rapid-Stirring Solvent Extraction Kinetic Technique

Simply expressed, under conditions of vigorous shaking<sup>5,11</sup> or high-speed stirring,<sup>12,13</sup> mass transfer rates in metal chelate solvent extraction processes are much greater than chemical reaction rates, particularly when, owing to favorable distribution characteristics, the concentration of one of the reactants is very low. It is axiomatic that, in any multistep process, the overall kinetics of the process gives information about the slowest, i.e., the rate-determining step. We have employed the classical Morton flask assembly<sup>14</sup> with stirring speeds of up to 20 000 rpm. Our apparatus<sup>12</sup> is always operated on the plateau of extraction rate vs. stirring speed, where further stirring energy does not reduce drop size of the dispersed phase but simply contributes to overall convective movement in the reaction flask. The data we obtain are highly reproducible and almost always result in simple experimental rate expressions having very nearly integral reaction orders. Furthermore, the values of chelation rate constants derived from the data are generally in accord

with those expected for the substitution rates of the metal ions and, where available from studies utilizing independent methods, in good agreement with the published values.

In contrast, most others interested in mass transfer kinetics in liquid-liquid distribution systems start by considering diffusion as the primary source of "resistance" and then include slow chemical reaction kinetics as added "resistances", usually without attempting to account quantitatively for the reaction rate constants. These workers tend to favor experiments in which the interfacial area is fixed. Fixed interfacial area designs<sup>15-20</sup> are rooted in the assumption that the reaction is either diffusion or interfacially controlled. Inasmuch as rate constraints of such reactions must be expressed in terms of unit interfacial area, fixed-interface experiments permit this measurement to be made. This has not been considered to be possible with high-dispersion experiments because the interfacial contact area is unknown. Most fixed-interface experiments have been performed with either a series of single drops in a continuous phase or a Lewis cell. In the drop method droplets of one phase are allowed to rise (or fall) through a column containing the second phase. This approach has been criticized for not overcoming diffusion effects in the droplet. The Lewis cell is designed so that both phases stand in contact with each other while each phase is stirred separately. Stirring supposedly overcomes diffusion problems by replenishing the interface with reactant from each bulk phase. Nevertheless, since the vigor of the stirring must be severely limited to avoid vortex formation, mass transfer effects are certainly not eliminated.

Extraction kinetics studies involving high dispersion involve vigorous shaking or stirring of the two phases.<sup>5,11,12,21-23</sup> These experiments are capable of attaining the fastest extraction rates. From the point of view of a mechanism in which a homogeneous chemical reaction is the rate-determining step, high dispersion is needed to reduce the time required for mass transfer processes so that diffusion effects are not involved in the observed reaction velocity and rate equations. In the case of an interfacial mechanism, a high dispersion maximizes the interfacial surface area, leading to a faster rate. Recently, Tavlarides<sup>24</sup> has critically reviewed most of the previous high-dispersion and fixed-interface experimental techniques and concluded each of them was seriously compromised.

One unequivocal way in which to resolve these controversies, or at least to validate our own experimental approach to extraction kinetics, would be to compare the values of the chemical reaction rate constants de-

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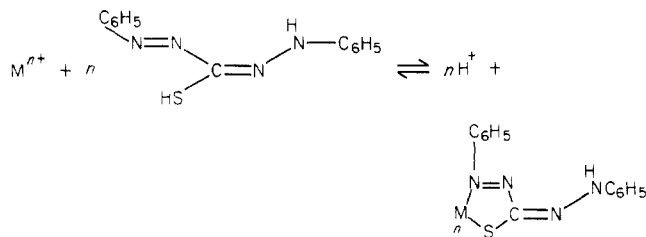
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rived from our experiments with those obtained elsewhere in the chemical literature. Yet another mode of resolution of these problems, particularly to clarify the role of the interface, would be to develop an experimental configuration in which results obtained with little or no interfacial region could be compared with those obtained with a large (and reasonably constant) interfacial region.

Recently, we have developed just such a measurement system that is based on the use of a selective Teflon phase separator that permits the sampling of the organic phase while it is still intimately mixed with the aqueous phase under high-speed stirring conditions.<sup>25</sup> With the help of this apparatus, we have studied the pH dependence of the equilibrium distribution of dithizone and a series of alkyl derivatives. We are able by these means to distinguish between those systems in which surface active components are present and those in which they are not. When they are present, quantitative evaluation of the role of the interface can be made.

### Dithizone Systems

Our studies began with an examination of the kinetics and mechanism of extraction of zinc(II) by dithizone.<sup>4</sup> A suitably buffered aqueous phase containing <sup>65</sup>Zn ( $C_{Zn} = 10^{-6}$  M) was shaken vigorously with a  $CHCl_3$  solution of dithizone and the radioactivity of the aqueous phase was determined at selected time intervals. The rate of extraction (loss in aqueous phase activity per second) was found to be first order in zinc concentration over several half-lives. Also, at shaking rates above a reasonable minimum, the rate of extraction was independent of this parameter.



When extractions were conducted at a series of pH and dithizone concentration levels, the pseudo-first-order rate constant was found to be precisely ( $\pm 10\%$ ) first order in dithizone concentration and inverse first order in  $[H^+]$ . With the aid of this experimental rate expression (eq 1), it was possible to select from the

$$\frac{d[Zn^{2+}]}{dt} = k' \frac{[Zn^{2+}][HDz]_0}{[H^+]} \quad (1)$$

following sequence of reaction steps: (a) mass transfer of ligand,  $HDz(o) \rightarrow HDz$ , (b) aqueous phase dissociation of ligand,  $HDz \rightarrow H^+ + Dz^-$ , (c) aqueous phase formation of 1:1 chelate,  $Zn^{2+} + Dz^- \rightarrow ZnDz^+$ , (d) aqueous phase formation of 1:2 chelate,  $ZnDz^+ + Dz^- \rightarrow ZnDz_2$ , (e) mass transfer of chelate,  $ZnDz_2 \rightarrow ZnDz_2(o)$ , step c as rate-determining (o designates the organic phase). The mass transfer steps a and e are rapid as indicated by the independence of the extraction rate from the shaking rate. Furthermore, experiments conducted in the presence of finely powdered glass to

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Table I  
Comparison of Second-Order Rate Constants for Formation of 1:1 Metal Chelates of Diphenylthiocarbazono (Dithizone) and of Di-*o*-tolylthiocarbazono with the First-Order Rate Constant of Water Dissociation of the Hydrated Metal Ions

metal ion	rate constant for water disson, <sup>26</sup> s <sup>-1</sup>	rate constant of ML <sup>+</sup> formation, M <sup>-1</sup> s <sup>-1</sup>	
		dithizone	di- <i>o</i> -tolylthizone
Cd <sup>2+</sup>	6.0 × 10 <sup>8</sup>	> 10 <sup>7</sup>	
Zn <sup>2+</sup>	5.0 × 10 <sup>7</sup>	6.1 × 10 <sup>6</sup>	7.5 × 10 <sup>6</sup>
Co <sup>2+</sup>	5.0 × 10 <sup>5</sup>	6.7 × 10 <sup>4</sup>	
Ni <sup>2+</sup>	2.0 × 10 <sup>4</sup>	1.3 × 10 <sup>3</sup>	5.2 × 10 <sup>3</sup>

increase the ratio of "wall" area to volume gave identical rate data, indicating that reaction on the walls of the container is not important. Another confirmation of the rapidity of step a was the observation that when  $CCl_4$  was substituted for  $CHCl_3$ , the increase in the rate of extraction quantitatively conformed to the change of  $K_{DR}$  of dithizone between the two solvents. First-order dependence on  $Zn^{2+}$  narrows the field to steps c or d. Inasmuch as the latter is not consistent with first-order ligand dependence, the homogeneous reaction of formation of the  $ZnDz^+$  complex is the slow step:

$$-\frac{dZn^{+2}}{dt} = k_1[Zn^{2+}][Dz^-] \quad (2)$$

Suitable substitution in eq 2 from the acid dissociation ( $K_a$ ) and Nernst distribution ( $K_D$ ) expressions

$$[Dz^-] = \frac{K_a[HDz]_0}{K_{DR}[H^+]} \quad (3)$$

gives the following expression

$$\frac{d[Zn^{2+}]}{dt} = \frac{k_1 K_a [Zn^{2+}][HDz]_0}{K_{DR}[H^+]} \quad (4)$$

By combining eq 4 and 1, when  $K_a/K_{DR}$  are known (from the pH dependence of the ligand distribution),  $k_1$  is obtained. For this reaction (eq 2), it is  $10^{6.6}$  M<sup>-1</sup> s<sup>-1</sup>, a value quite in accord with typical Zn-substitution rate constants.

With the help of eq 3, we see how the problem of measuring the kinetics of inherently rapid reactions can be simply solved by the solvent extraction technique. For example, the value of  $K_a/K_{DR}$  for dithizone in chloroform is  $10^{-10.6}$ . This is the factor that transforms  $k_1$  to the smaller and much more accessible  $k'$  of eq 1. Moreover, the solvent extraction kinetic technique has the virtue of capability of dealing with systems involving highly water-insoluble species. Indeed, for dithizone and its metal chelates, there is no alternative experimental approach to the study of the kinetics of formation. For this reason, we undertook a systematic study of the mechanism of formation of metal chelates of these interesting sulfur-containing ligands.

Subsequent studies<sup>11</sup> of rates of extraction of divalent Cd, Co, and Ni dithizonates from buffered aqueous solutions by chloroform solutions of dithizone were also found to follow eq 2. That the mechanism of chelate formation is related to dissociation of water from coordination with the metal ion can be seen from comparison of our data with those obtained by Eigen (Table I). The rates of these two reactions differ by an almost

(26) Eigen, M. *Pure Appl. Chem.* 1963, 6, 97.

constant factor (ca. 10-fold).

The rate constants obtained for  $Zn^{2+}$  and  $Ni^{2+}$  with di-*o*-tolylthiocarbazono differ significantly from those with the parent, dithizone (Table I), and in fashion not parallel with the corresponding chelation equilibrium constants.<sup>27</sup> With the latter, a 50-fold decrease in  $ZnL^+$  formation constant of the di-*o*-tolyl derivative is observed. That no such drop is seen in the rate constant demonstrates that a two-step mechanism, i.e., where  $k_1 = Kk$ , is involved. There is either a rapid preequilibrium of an outer sphere complex<sup>28</sup> or one in which an inner sphere complex is involved. In the latter case, although  $K$  would be reduced by the steric hindrance of the *o*-methyl group, the weakening of the  $M-H_2O$  bond in the complex due to steric hindrance would bring about a compensating rise in  $k$ .<sup>11</sup>

The validity of the interpretation that chelate formation in the aqueous phase is the rate-determining step was further confirmed when rate constants obtained by the solvent extraction technique for the  $Ni^{2+}$ -phen<sup>29</sup> and  $Ni^{2+}$ -8-quinolinol<sup>7</sup> systems were found to be in good agreement with values obtained by stop-flow techniques.

The extraction kinetics of dithizone derivatives, studied in some detail, are here summarized. In every case studied, the rate-determining step was identified as the formation of the 1:1 metal complex in the aqueous phase. Even though the proton affinity (as measured by  $pK$ ) of the ligands could be altered predictably by the introduction of substituents of given electronegativity (as measured by the Hammett  $\sigma$  value), the rates of formation the corresponding  $Zn^{2+}$  or  $Ni^{2+}$  complexes were enhanced by both electron-releasing and -withdrawing substituents.<sup>30</sup>

These reactions were characterized by a surprisingly large negative activation entropy.<sup>31</sup> When auxiliary ligands such as acetate, thiocyanate, etc. were present in the aqueous phase prior to extraction and formed 1:1 metal complexes, these were found to react more rapidly with dithizone than did the hydrated ions,<sup>32</sup> lending strength to the general perception that the first coordinated water is the hardest to remove in metal ligand substitution reactions.

This work also provided a novel and independent method for the determination of formation equilibrium constants for the acetate, thiocyanate, and other metal complexes. Finally, with use of  $NiDz_2$  in  $CHCl_3$  as a model system for studying back-extraction (or stripping) kinetics,<sup>33</sup> we found that Lewis acids having affinity for the  $-S-$  grouping significantly catalyzed the stripping, probably because they reacted with the chelate directly rather than subsequent to the partial chelate dissociation required by  $H^+$  attack. Cyanide, which probably can axially coordinate with  $Ni$  in the  $NiDz_2$ , was found to be more kinetically effective than EDTA, which like  $H^+$ , requires prior chelate dissociation.

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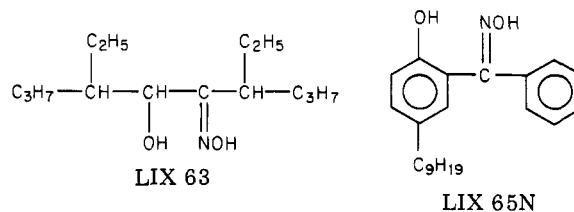
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## High Molecular Weight Hydroxy Oxime Systems

Recently, we turned our attention to a detailed study of the kinetics of extraction of  $Cu(II)$  with aromatic and aliphatic hydroxy oximes, symbolized LIX, which were introduced in the 1960s by General Mills for the large-scale extraction of copper.<sup>34</sup> Our earlier work suggests that with extractants of higher molecular weight and hence of larger  $K_{DR}$  values, the observed rates of inherently faster reactions, e.g., those of  $Cu^{2+}$ , would become accessible to the solvent extraction technique. Furthermore, the kinetics of  $Cu$ -LIX extractions are of great practical importance and had already been the subject of some study. Our interest in these systems was enhanced by the widespread claim that the mechanism of such systems, unlike those we studied, involves a slow, interfacial reaction.<sup>21-23</sup>

Most of the theoretical studies have been performed with 2-hydroxy-5-nonylbenzophenone oxime (LIX65N) and 5,5-diethyl-7-hydroxydodecan-6-one oxime (LIX63).



Previous workers, pointing to the low aqueous solubility of the LIX reagents, almost invariably discarded the possibility of chelate formation in the aqueous phase and proposed that interfacial reaction kinetics, rather than homogeneous chemically controlled rates, are dominant. Thus, in a review of the kinetics and mechanisms of  $Cu(II)$  extraction by LIX reagents, Flett<sup>35</sup> asserted that because these reagents are "so hydrophobic", their aqueous phase solubility could be ignored! Having adopted this stance, when chemical parameters appeared in the extraction rate expressions, these investigators invoked an "interfacial reaction" as the rate-determining step.

First, we determined the distribution equilibrium of LIX 65N between chloroform and water to be  $10^{4.6 \pm 0.3}$ ,<sup>13</sup> which is significantly less than that of dithizone (vide supra). On the basis of our kinetic data, the rate expression for the extraction of copper by LIX 65N can be quantitatively described by eq 5, where HL repre-

$$-\frac{d[Cu^{2+}]}{dt} = k' \frac{[Cu^{2+}][HL]_0^2}{[H^+]} \quad (5)$$

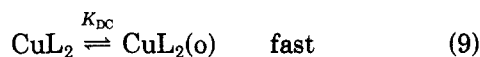
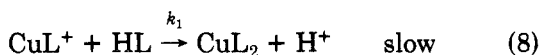
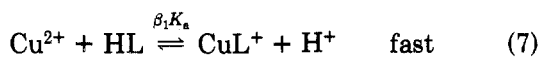
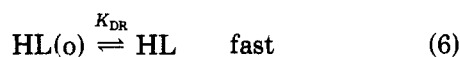
sents LIX 65N. It is noteworthy that all of the experimentally observed kinetic orders are integral.

The extraction of copper by LIX 65N is unusual in that the observed second-order dependence on ligand concentration contrasts sharply with the nearly universally observed first-order ligand dependencies.<sup>40</sup> This behavior is not unique, however, since for  $d^9$  metal ions the rate constants for the 1:1 and 1:2 complexes are not as different as they are for most other transition-metal ions.

(34) Swanson, R. R. U.S. Patents 3 131 998, May 1964; 3 224 873, Dec 1965; 3 428 449, Feb 1969.

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From the observed second-order ligand dependence on the rate of extraction, it follows that in this system the rate-determining step is the reaction of  $\text{CuL}^+$  with HL (eq 8)



where  $K_{\text{DR}}$  and  $K_{\text{DC}}$  represent the distribution constants of ligand and chelate,  $K_a$  the acid dissociation constant of LIX 56N, and  $\beta_1$  the equilibrium formation constant of  $\text{CuL}^+$  from  $\text{Cu}^{2+}$  and  $\text{L}^-$ . The overall extraction rate, under conditions where extraction is essentially complete at equilibrium, is determined by the rate of step 8, as given by eq 10. By substituting appropriate

$$-\frac{d[\text{Cu}^{2+}]}{dt} = k_1[\text{CuL}^+][\text{HL}] \quad (10)$$

equilibrium expressions from eq 6 and 7 into eq 10, one obtains eq 11, in which the observed dependence on

$$-\frac{d[\text{Cu}^{2+}]}{dt} = \frac{k_1 \beta_1 K_a [\text{Cu}^{2+}][\text{HL}]^2}{K_{\text{DR}}^2 [\text{H}^+]} \quad (11)$$

metal ion, ligand, and pH are explained. Further, the observed reaction rate constant,  $k'$ , is seen to be given in eq 12.

$$k' = k_1 \beta_1 K_a / K_{\text{DR}}^2 \quad (12)$$

Although, unfortunately, the formation equilibria of Cu-LIX 65N have not been studied, a reasonable approximation of  $\beta_1 K_a$  (to within about 1 order of magnitude) can be estimated from values obtained with salicylaldoxime, a closely related ligand. In fact, inasmuch as within a given ligand family, changes in  $\beta_1$  tend to be compensated by counterchanges in  $K_a$ , the product tends to remain relatively constant (with a noticeable but small increase with increasing  $K_a$ ). Hence from the measurement of  $\beta_2 K_a$  for salicylaldoxime and  $\text{Cu}^{2+}$  of  $10^{4.2}$ ,<sup>36</sup> we may take  $\beta_1 K_a$  as  $10^{2.0}$ , inasmuch as  $\beta_1$  is approximately  $\beta_2^{1/2}$ . Together with the value of  $K_{\text{DR}}$  as  $10^{4.6}$  and  $k'$  of 1.37,  $k_1$  for LIX 65N is reckoned to be  $2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , a value that is quite similar to rate constants for typical substitution reactions of  $\text{Cu}^{2+}$  (the corresponding rate constant for Cu and phenanthroline is only 3 times larger).<sup>37</sup>

This agreement with generally observed rate constant for copper substitution reactions in aqueous media represents strong evidence for the mechanism of the Cu-LIX 65N extraction developed here. If chemical reactions at the interface were significant, far larger apparent rate constants would be calculated.

Even more convincing proof of the mechanism described above can be obtained by testing the validity of eq 12, using a series of organic solvents in parallel rate studies. Thus, Akiba and Freiser<sup>38</sup> found the ob-

served rate of extraction of copper with LIX 65N,  $k'$ , to vary by 3 orders of magnitude when seven organic solvents ranging from trichloromethane to *n*-heptane were used. The variation of  $\log k'$  with  $\log K_{\text{DR}}$  was linear and had a slope of -2, as required by eq 12. Similarly, in the case of the extraction kinetics of nickel with LIX 65N, which was found to be first order in ligand, the value of the slope of the log-log line of  $k'$  vs.  $K_{\text{DR}}$  is unity, in keeping with the mechanism having as the rate-determining step the formation of  $\text{NiL}^+$  in the aqueous bulk phase.<sup>38</sup> The exact correspondence of variation of the observed rates to inverse first (with Ni) and second (with Cu) orders of the ligand distribution constants with the same set of solvents rules out any possible influence of interfacial effects in these systems.

### Interfacially Active Extractant Systems

This should not be taken to mean that an interfacial influence on extraction kinetics conducted under high-speed stirring conditions will never occur. Indeed, we set about to search for systems in which just such effects could occur by preparing and studying a series of symmetrically dialkylated dithizones, from methyl to hexyl. It seemed appropriate to start with derivatives of the extractant having the highest  $K_{\text{DR}}$  of all of the extractants studied to date. With use of the automated extraction apparatus,<sup>25</sup> at high pH values, a drop in the alkylated dithizone concentration in chloroform was observed; it varied with stirring speed up to a plateau region. The extent of the decrease in concentration varied with pH at stirring speeds in the plateau region in a manner parallel to the nonstirring experiment. That permitted us to obtain the  $\text{pH}_{1/2}$  (pH at which 50% of the ligand remains in the organic phase). The difference in  $\text{pH}_{1/2}$  values (stirring vs. no stirring) increased from 0.16, 0.66, 3.0, and 5.0 as the alkyl group varied from methyl to ethyl, to butyl, to hexyl while no such change was observed with dithizone itself.

Interfacial tension measurements were carried out with aqueous phases at two pH values, 3.5 and 12.0, and the following organic phases: Dz in  $\text{CHCl}_3$ , BuDz in  $\text{CCl}_4$ , and BuDz in  $\text{CHCl}_3$ . In the acidic systems, there was no change in  $\gamma_i$  value that could be attributed to the presence of the solute. In the alkaline systems, however, a decrease in  $\gamma_i$  was observed with increase of solute concentration. The maximum slopes of these curves were used to estimate the surface area occupied by one solute molecule, A, according to Gibbs adsorption isotherm

$$A = -kT / (\delta\gamma_i / \delta \ln C)_T$$

where  $k$  is the Boltzman constant and  $C$  is the concentration of solute. The estimated values for A ( $\text{\AA}^2/\text{molecule}$ ) were 90 for Dz in  $\text{CHCl}_3$ , 70 for BuDz in  $\text{CCl}_4$ , and 150 for BuDz in  $\text{CHCl}_3$ . The minimum solute concentration required for interfacial saturation,  $C_m$ , can also be estimated; the values for  $\log C_m$  were -2.2 for Dz in  $\text{CHCl}_3$ , -3.7 for BuDz in  $\text{CCl}_4$ , and -2.8 for BuDz in  $\text{CHCl}_3$ . As might be expected, the greater effect is observed in the poorer solvent. The decrease in interfacial tension under alkaline but not acid conditions suggests that it is the reagent anion rather than the nonionized reagent that is surface active.

(36) Sillen, L. G., Martell, A. E., Ed. "Stability Constants of Metal Ion Complexes"; Chemical Society: London, 1964; Spec. Publ. 17.

(37) Wilkins, R. G. "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974.

(38) Akiba, K.; Freiser, H. *Anal. Chim. Acta* 1982, 136, 329.

The reversible concentration change in organic phase, which was caused by stirring, suggests a significant participation of the liquid-liquid interface in the equilibrium. The interfacial component is less than 3% for dithizone and then rises rather rapidly from 26% in MeDz to 82% in EtDz, to 99.9% in BuDz, and to all but  $7 \times 10^{-4}\%$  in hexyldithizone. These changes are indicative of the dramatic change in the heterogeneous acid-base equilibrium constant (up to a factor of  $10^5$ ) that occurs because the anionic alkylidithizonate (but not the neutral ligand) is surface active and is adsorbed into the interfacial region.<sup>39</sup>

The extraction kinetics of nickel and zinc with the alkylidithizonates<sup>39</sup> closely resembled those with dithizone and its analogues studied earlier,<sup>30</sup> in that the rate was first order each in metal and ligand and inverse first order in hydrogen ion. However, if one were to assume that the mechanism remained the same, i.e., that the rate-determining step was the formation of the 1:1 complex from metal and ligand anion in the aqueous phase, one would estimate increases in the second-order reaction rate constant with increasing size of alkyl group until, with the hexyldithizone, the values for both Ni and Zn would exceed the diffusion-limited rate constant for bimolecular reaction!

(39) Watarai, H.; Freiser, H. *J. Am. Chem. Soc.* 1983, 105, 191.

(40) Watarai, H.; Freiser, H. *J. Am. Chem. Soc.* 1983, 105, 189.

Having determined from the effect of stirring that the ligand anion is concentrated in the interface, however, one can reasonably assume that the locus for the formation of the 1:1 complex is the interfacial region. Calculating the correct value of the ligand anion concentration in the interface from the observed differences in  $\text{pH}_{1/2}$  values (vide supra) and assuming that since the metal ion is not surface active, its concentration in the interface is the same as it is in the bulk aqueous phase, we obtained values for rate constants that were eminently reasonable, i.e., essentially constant values for all the alkylated dithizonates.  $\log k_1$  for Ni and Zn are 5.13 and 8.08, respectively, which are consistent with those obtained for these metals in a broad cross section of ligand-substitution reactions. Essentially the entire cause of the unusual kinetic behavior, as well as of the unusual extraction equilibrium behavior, is the excess concentration of the ligand anion in the interfacial region, which is greatly enlarged by high-speed stirring.

Our studies are now directed toward characterizing the nature and the behavior of unsupported liquid-liquid interfaces, as well as the chemical reactions that occur in such an environment, an area of research that seems certain to be of significance to surface science in general as well as to extraction chemistry in particular.

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## Photobehavior of Alkyl Halides in Solution: Radical, Carbocation, and Carbene Intermediates

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One of the most conceptually simple and earliest studied chromophores is that of the carbon-iodine bond. The lowest lying transition involves promotion of one of the n electrons of iodine to the  $\sigma^*$  orbital of the bond. Since an antibonding orbital is now occupied and the transition occurs at an energy ( $\sim 380$  kJ/mol) far exceeding the carbon-iodine bond strength ( $\sim 215$  kJ/mol), it is not surprising that the bond undergoes efficient light-induced cleavage. From extensive early studies, conducted principally in the gas phase, it was demonstrated that the absorption of light by an alkyl iodide leads to homolytic cleavage of the carbon-iodine bond (eq 1) followed by ground-state reactions of the resulting alkyl radical and iodine atom.<sup>1,2</sup> In some cases molecular  $\beta$  elimination of HI (eq 2) was proposed as a competing minor pathway.<sup>3</sup>



Studies on the photobehavior of alkyl iodides in the liquid phase and in solution came later.<sup>4</sup> Once again the results were generally interpreted in terms of radical intermediates. It was here, however, that anomalous results began to appear, such as the isomerization of 1-iodopropane (1) to the 2-iodo isomer 2 and the formation of 2-butene (4) from 1-iodo-2-methylpropane (3).<sup>5</sup> Alkyl radicals do not normally undergo the type

(1) For an early review of the photobehavior of alkyl halides, see: Steacie, E. W. R. "Atomic and Free Radical Reactions", 2nd ed.; Reinhold: New York, 1958.

(2) For a more recent review of the gas phase photobehavior of alkyl halides, see: Majer, J. R.; Simons, J. P. *Adv. Photochem.* 1964, 2, 137-181.

(3) See: Thrush, B. A. *Proc. R. Soc. London, Ser. A* 1958, 243, 555-560. Schindler, R.; Wijnen, N. H. *J. Z. Phys. Chem. Neue Folge* 1962, 34, 109-112.

(4) For a recent review of the solution phase photobehavior of alkyl halides, see: Sammes, P. G. In "Chemistry of the Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: New York, 1973; Chapter 11.

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