JOURNAL OF CATALYSIS **93**, 209–215 (1985)

Catalysis of Deuterium Transfer between Liquid Chloroform and Water by Anion-Exchange Resins[1]

E. ALLAN SYMONS[2] AND J. DOUGLAS BONNETT

Physical Chemistry Branch, Atomic Energy of Canada Limited, Research Company,
Chalk River Nuclear Laboratories, Chalk River, Ontario K0J 1J0, Canada

Received October 10, 1984

Anion-exchange resins in the hydroxide form have been successfully utilized for catalysis of deuterium transfer between water and liquid chloroform under stirred three-phase slurry conditions. In-solution rate constants for $CDCl_3/H_2O$ exchange obtained at 15–35°C with *liquid* chloroform and 0.10 mol/liter NaOH solution under stirred conditions are in good agreement with literature data measured in the absence of bulk chloroform. At 25°C the resins tested, Rexyn 201(OH) and Ionac ASB-1P(OH), are ~25× more effective per mole of ^-OH present than NaOH when they are used as whole beads. A further improvement is observed if the beads are crushed, but the latter state would be less suitable for commercial-scale application. The solubility of chloroform in the aqueous phase under isotope-exchange conditions was required to calculate the in-solution rate constants for exchange. A method was developed to obtain chloroform solubilities in 0.10 mol/liter NaOH solution and aqueous resin slurries; equilibrated solution samples were treated with 1 mol/liter NaOH to hydrolyze the dissolved $CHCl_3$ to chloride ion, which was then analyzed by specific ion electrode.

INTRODUCTION

Laser-induced multiple photon dissociation of the C–D or C–T bond in haloalkanes has been proposed as the basis of a process for separation of hydrogen isotopes (*1*). Fluoroform has received the most attention (*1–3*), but other gaseous trihalomethanes like dichlorofluoromethane (*4*) and chlorodifluoromethane (*5*) have also been studied in detail.

An important part of the overall isotope separation process involves exchange of the particular isotope (deuterium or tritium) from a feedwater stream to the depleted haloalkane before the latter is recycled to the laser photodissociation stage. Some form of catalyst is necessary to promote the isotope-exchange step, and for fluoroform rather extreme conditions have had to be proposed: the use of 1 mol/liter NaOH solution at 120°C (*6*); or, the addition of dimethyl sulfoxide as cosolvent to obtain reasonable exchange rates with NaOH at lower concentration and temperature (*7*); or, the inclusion of an intermediate liquid–liquid transfer stage to utilize more efficient isotope-exchange reactions (*2*). Under these alkaline conditions the hydrolysis of the trihalomethanes can be a serious problem, but as yet no effective exchange catalyst other than aqueous hydroxide ion has been identified. For fluoroform the hydrolysis reaction becomes significant above 120°C (*6*), although at 60–80°C deuterium exchange was found to be a factor of ~10^4 faster than hydrolysis (*8*). However, for the dichlorofluoro- and chlorodifluoromethane systems the situation is worse, since hydrolysis occurs readily and competes with isotope exchange (*5, 9, 10*).

More recently there has been interest in the laser photochemistry of chloroform (*11, 12*), particularly regarding recovery of tritium from contaminated light and heavy-water moderator in nuclear power reactors

---

[1] AECL Report No. 8725

[2] To whom correspondence should be addressed.

0021-9517/85 $3.00

(*11*). Base-catalyzed deuterium exchange between chloroform and water is known to be relatively fast even at 0°C (*13*) and fortunately the hydrolysis reaction is a factor of $>10^4$ slower at this temperature (*13*). With a view to the application of supported catalysts to the chloroform–water system on an industrial scale we have studied the effectiveness of anion-exchange resins under two-liquid-phase conditions at 15–35°C. The usual problem of thermal instability of organic resins above 100°C (*6*) does not arise. Because our primary kinetic data for isotope exchange refer to change in the $CDCl_3/CHCl_3$ composition of the *bulk* chloroform phase, we needed to measure the solubility of chloroform in the aqueous phase in order to calculate in-solution rate constants.

EXPERIMENTAL

Chloroform solubility. The solubility of $CHCl_3$ in water as a function of temperature has been well documented (*14*). However, we required values for dilute NaOH solution and resin slurries, where slow hydrolysis of the chloroform adds a complication to the measurement of solubility. A method has been developed that takes advantage of this reaction, wherein the dissolved $CHCl_3$ is intentionally converted to chloride ion for analysis by specific Cl^- electrode.

The method was first tested with pure water, to ensure that reliable data could be obtained. Liquid $CHCl_3$ was contacted with deionized, distilled water in a round-bottom flask modified with inside fins and a septum arm. The flask was rotated gently at a 45° angle in a constant temperature bath for at least 1 h, by means of a rotary evaporator assembly, to achieve equilibration. With this approach the emulsions obtained when the two phases were vigorously stirred could be avoided. The phases were allowed to separate, and triplicate 5.0-ml samples of the clear aqueous phase were transferred by syringe to 25.0 ml of 1.2-mol/liter NaOH solution. These solutions were heated at 70°C for 10 min with agitation. Based on the work of Hine *et al.* (*10*), the in-solution half-life for hydrolysis is <10 s at 70°C. Heating times of 20 and 30 min did not lead to significant change in the measured $[Cl^-]$.

The hydrolyzed samples were neutralized with 1.0 mol/liter HNO_3 and diluted with water to produce a solution of ionic strength 0.10 mol/liter. The $[Cl^-]$ was determined directly with an Orion Research 96-17B combination Cl^- electrode/Model 701A Ionalyzer. The electrode was calibrated before and after each set of unknowns with aqueous NaCl standards adjusted to ionic strength 0.10 mol/liter with $NaNO_3$ solution. Sodium formate, a chloroform hydrolysis product, was checked for possible interference with electrode operation; no problem was found.

The same general procedure was employed for $CHCl_3$ solubility in 0.10 mol/liter NaOH solution. At the same time that analysis samples were withdrawn from the equilibration flask an additional sample was taken, neutralized immediately with HNO_3, and diluted to 50 ml with water and enough $NaNO_3$ solution to provide 0.10 mol/liter ionic strength. This sample served as a background correction for Cl^- generated by slow hydrolysis during the equilibration period. The correction ranged from 0.5 to 10% of the gross Cl^- measured at 15 to 35°C. The background correction for pure water was negligible.

For the three-phase slurries, samples of the clear aqueous phase were taken for analysis.

Deuterium-exchange runs. $CDCl_3$ (99.8 atom% D) was obtained from MSD Isotopes, Montreal; $CHCl_3$ was reagent grade solvent from Fisher Scientific. Standard NaOH solutions were prepared from concentrates with deionized, distilled water. Rexyn 201(OH) (Fisher Scientific) and Ionac ASB-1P(OH) (Ionac Chemical Company, Birmingham, N.J.) ion-exchange resins were used as received.

One of our Pyrex stirred gas/liquid reactors (*8*) was modified to permit withdrawal of homogeneous liquid samples of the reaction emulsion. An 18-gauge syringe needle was mounted through a sidearm septum and supported vertically along the inside wall by a Teflon retaining ring; the side port sampling hole, located 1 cm from the bottom of the vessel, was made as large as possible to minimize selective removal of water relative to chloroform.

The two-phase runs were carried out at constant temperature (±0.10°C) with 45 ml of NaOH solution and 15 ml of $CDCl_3$ (all components weighed). For the three-phase runs 45 ml of water, 15 ml of $CDCl_3$, and 1–7 g of wet ion-exchange resin were used. The resin beads were tested in both the whole and crushed states. Dry N_2 was added at ~110 kPa to facilitate sample removal by syringe, and the systems were stirred at ~750 rpm to ensure homogeneous mixing of the liquid phases. Kinetic samples (1 ml) of emulsion were taken by syringe through a Mininert push-button valve and immediately put into stoppered small glass tubes containing enough acid solution to neutralize the base catalyst. After each chloroform layer had settled it was transferred by syringe through a septum into one of a set of small evacuated tubes for deuterium analysis.

Deuterium content of the chloroform was determined by mass spectrometry on vapor samples expanded from the analysis tubes, which contained 0.15–0.25 ml of liquid. The intensities of peaks at $m/e = 12(^{12}C^+)$, $13(^{13}C^+, H^{12}C^+)$, $14(D^{12}C^+, H^{13}C^+, ^{14}N^+)$, and $28(^{14}N_2^+)$ (from residual air in the samples) were obtained on a CEC 21-614 Residual Gas Analyzer. Corrections were then made for ^{13}C at $m/e = 13$ and 14, and for ^{14}N at 14, based on the $^{14}N^+/^{14}N_2^+$ instrument response over the same N_2 pressure range. To allow for any vapor pressure isotope effect occurring in the analysis tubes or instrument, each $D^{12}C^+/(D^{12}C^+ + H^{12}C^+)$ ratio was corrected by a calibration curve that was constructed from a set of five $CDCl_3/CHCl_3$ standards prepared by weight.

Pseudo-first-order plots of ln(% $CDCl_3$) versus time give the rate constant for change in the D/H ratio for the *bulk* chloroform in the reaction vessel, k_{obs} (bulk). These observed rate constants must be multiplied by the conversion factor [total moles chloroform in system/moles chloroform dissolved in the aqueous phase] to obtain k_{obs} (solution) data comparable to Hine *et al.*'s results (*15*). The $CHCl_3$ solubility data were used to calculate this factor as a function of reaction conditions. The factor will be constant during a run if the solvent composition of the kinetic samples withdrawn from the reaction vessel does not change.

Chloroform hydrolysis. The temperature dependence of chloroform hydrolysis in NaOH solution has been well studied (*10*). However, the hydrolysis rate under stirred "three-phase" resin slurry conditions was needed for direct comparison with the corresponding isotope-exchange data.

Hydrolysis runs were carried out at 25 and 35°C with 15 ml $CHCl_3$ (or $CDCl_3$, to confirm resin still active for isotope exchange), 45 ml H_2O, and 5 g whole Ionac ASB-1P(OH) resin beads. Periodically the stirrer was stopped and 1-ml samples of the aqueous phase were removed for analysis of Cl^- by specific ion electrode. Because hydrolysis was found to be so slow under these conditions (<1% reaction after 90 h at 25°C), only upper limit values of k_{obs} could be estimated.

RESULTS

$CHCl_3$ Solubilities

At 25°C the best fit literature value for $CHCl_3$ solubility in water is 0.792 wt% ($=6.63 \times 10^{-2}$ mol/liter) (*14*). Our results from two experiments, each the average of measurements on three samples, are 6.56 ± 0.16 and $6.60 \pm 0.12 \times 10^{-2}$ mol/liter. The temperature dependence of $CHCl_3$ solubility is shown in Fig. 1 over the range 15 to 35°C. The data obtained by the present hydrolysis method are in good agreement, within ±2–3%, of the best fit-literature data line (*14*). An experimental uncertainty of ±3% is therefore assigned to our solubility data.

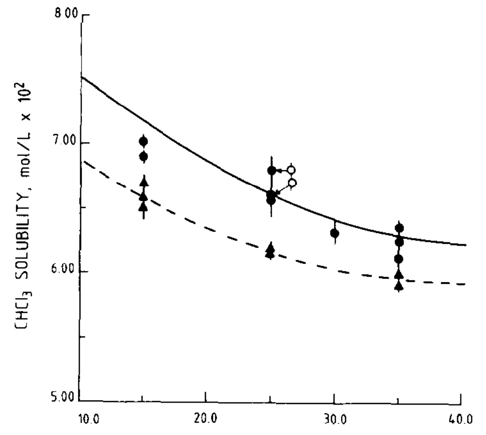

FIG. 1. Temperature dependence of chloroform solubility in some aqueous systems: (●) distilled water; (▲) 0.10 mol/liter NaOH solution; (○) clear aqueous phase after contact with anion-exchange resin (see text). The solid line is from the equation reported for best fit of literature data (*14*) for water. The dashed line has been drawn with similar curvature through the NaOH solution data.

In the presence of 0.10 mol/liter NaOH the chloroform is salted out of solution by 6–8% over the same temperature range (Fig. 1). For the anion-exchange resin bead slurry, not surprisingly the $CHCl_3$ solubility in the aqueous phase surrounding the beads is the same as for pure water, within experimental error. However, the chloroform concentration in the polystyrene matrix of the porous beads may be higher than in the bulk water, by analogy with the fluoroform/aqueous resin slurry case (*16*).

$CDCl_3/H_2O$ Isotopic Exchange

The kinetic plots for homogeneous NaOH catalysis of $CDCl_3/H_2O$ exchange were quite linear for 1–3 half-lives. Based on $CHCl_3$ solubility in the 0.10 mol/liter NaOH solution (Fig. 1), and assuming a negligible $CDCl_3/CHCl_3$ solubility isotope effect, the following bulk chloroform phase → aqueous solution phase conversion factors (see Experimental) were calculated: 63.5 at 15.4°C, 67.6 at 25°C, and 70.1 at 34.6°C. The k_{obs} (solution) values determined for $CDCl_3$ exchange are plotted in Fig. 2 together with points obtained by extrapolation of Hine *et al.*'s data (*17*) at 0°C—4.70×10^{-4} s^{-1} for 0.10 mol/liter NaOH and E_a = 100.5 kJ/mol (24.0 kcal/mol). From the slope of the least-squares line for our data in Fig. 2 we obtain E_a = 99.6 ± 5 kJ/mol. The very good agreement with Hine's results obtained under single-phase conditions confirms that mass transfer effects were not important under our stirred emulsion conditions.

After infinity correction the kinetic plots for ion-exchange resin runs with whole beads tended to show an initial downward curvature that was not present for the crushed bead or NaOH-catalyzed runs. This initial rate increase probably arises from the setting up of the chloroform/water equilibrium in the bead pores. At the end of these runs the initially clear solutions were usually cloudy and particle fines were present, although only a small fraction of the beads had fractured. The different types and batches of resin varied in their resistance to bead failure. One batch of Rexyn

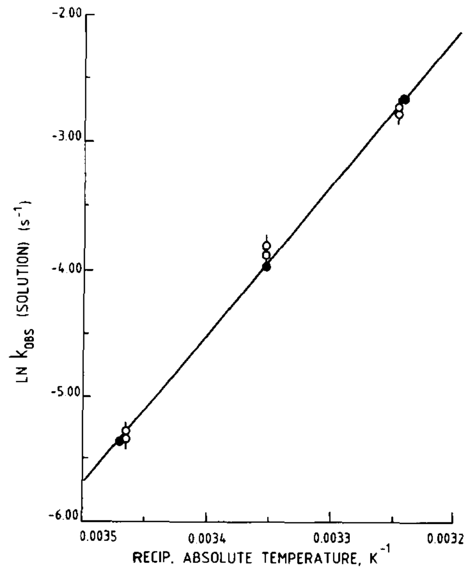

FIG. 2. Comparison of rate constants for $CDCl_3/H_2O$ exchange catalyzed by 0.10 mol/liter NaOH under (○) two-phase (this work) and (●) single-phase (Ref. (*17*)) conditions; ±10% bars shown.

TABLE 1

A Comparison of NaOH and Anion-Exchange Resin ($^{-}$OH Form) Reactivities for $CDCl_3/H_2O$ Deuterium Isotope Exchange at 25°C under Two-Phase Conditions[a]

Catalyst	k_{obs} (solution) (s^{-1})	k_{obs}/mol of $^{-}$OH[b]
NaOH, 0.10 mol/liter	0.195×10^{-1}	4.3
Rexyn 201(OH) beads, whole[c]	2.8×10^{-1}	31
Rexyn 201(OH) beads, crushed[d]	3.5×10^{-1}	39
Ionac ASB-1P beads, whole[e]	2.6×10^{-1}	24
Ionac ASB-1P beads, crushed[d]	$10. \times 10^{-1}$	95

[a] 15 ml chloroform, 45 ml aqueous phase; 5 g wet resin.

[b] Moles of hydroxide ion in reaction vessel.

[c] $^{-}$OH loading 1.7 mmol/g wet resin.

[d] Beads crushed with mortar, not sieved, particle size range not measured.

[e] $^{-}$OH loading 2.0 mmol/g wet resin.

201(OH) disintegrated completely when used under stirred conditions.

Both the Rexyn 201 and Ionac ASB-1P resins showed a significant increase in exchange reactivity when they were used in a crushed state, a reflection of the greater accessibility of the catalytic sites. Reproducibility between resin runs was generally poorer than for the NaOH runs, presumably because of easier deactivation of the catalyst by CO_2 in the air during handling. Representative results for the resin runs are recorded in Table 1; for the above reason, the maximum values determined under identical conditions are given. The k_{obs} were proportional to the weight of resin used, over the range 1 to 5 g.

Chloroform Hydrolysis in the Resin Slurries

Catalysis of chloroform hydrolysis by NaOH is $\sim 1.4 \times 10^4$ times slower than deuterium exchange at 0°C (*10, 13, 15*). Corresponding results for the Ionac ASB-1P anion-exchange resin are as follows: at 25°C the hydrolysis was barely detectable after 90 h, so that $k_{obs} < 1 \times 10^{-7}\ s^{-1}$ and the ratio $k_{exchange}/k_{hydrolysis}$ is $>1 \times 10^6$.

Even at this relatively large ratio, if hydrolysis did become significant on the long-term scale of an industrial process, there is good evidence that the addition of chloride ion to the aqueous phase will suppress the hydrolysis reaction (*18*).

DISCUSSION

For catalysis of CDF_3/H_2O isotopic exchange (*16*), a marked improvement in catalytic activity relative to NaOH was noted for the hydroxide ion when it is supported on anion-exchange resin beads. A similar effect has been observed in the $CDCl_3/H_2O$ system; rate constants per mole of $^{-}$OH present are compared in Table 1 for the resins and NaOH. The enhancement apparently arises from an increased haloform concentration in the styrene–divinylbenzene network of the polymer near the catalytic sites. Crushing the beads leads to faster access to the catalytic sites, by reducing the diffusion distance for the chloroform molecules to the hydrated $^{-}$OH ions. The observed effect is greater for the Ionac resin. From an industrial scale point of view the whole beads would be easier to handle as a supported/supportable catalyst than the crushed beads.

Anion-exchange resins will also be effective for catalyzing transfer of *tritium* between water and chloroform. For removal of tritium from the coolant of light-water reactors the exchange reaction of interest is

$$HTO + CHCl_3 \overset{K_1}{\rightleftarrows} H_2O + CTCl_3 \quad (1)$$

whereas for heavy-water reactors the reaction is

$$DTO + CDCl_3 \overset{K_2}{\rightleftarrows} D_2O + CTCl_3. \quad (2)$$

In each case the tritium-enriched chloroform would be recycled to the laser section of a plant designed to recover the tritium photochemically (*11*). These reactions involve transfer of tracer-level tritium *from water,* so that although a C–H bond is broken in (1) and a C–D bond in (2) the rate-limiting step for both will be cleavage of a C–T bond (*19*).

Rate constants for H exchange can be estimated from the corresponding D data and the primary kinetic isotope effect; k_D/k_T determined for homogeneous NaOH-catalyzed reaction should be applicable. For k_{2D} (the second-order in-solution rate constant) at 25°C a mean value derived from Fig. 2, which includes points obtained by extrapolation of Hine's data (*18*), is 0.195 liter/mol/s. Literature values reported for detritiation of $CTCl_3$ (tracer-level tritium) at 25°C are $k_{2T} = 0.165$ (*20*) and 0.163 liter/mol/s (*21*). Therefore $k_D/k_T = 1.19 \pm 0.003$, and $k_H/k_D = (k_D/k_T)^{2.344}$ (*22*) $= 1.50 \pm 0.07$. Margolin and Long (*20*) obtained the value 1.42 ± 0.01 for k_H/k_D by measuring directly the relative rates of tritium uptake by $CHCl_3$ and $CDCl_3$ with NaOH as catalyst.

Based on our data in Table 1, the half-life for T transfer from water in reaction (1), with Ionac ASB-1P(OH) whole beads as catalyst, will be ~2 s at 25°C, for a loading of 5 g resin/45 ml water. For reaction (2) the base will in fact be resin ^-OD in D_2O, which is a slightly more basic system as measured by the solvent isotope effect; reactivity for H removal runs as much as 50% higher for $^-OD/D_2O$ than for $^-OH/H_2O$ (*13*, *23*). Thus for reaction (2) at 25°C with the Ionac resin an in-solution half-life of ~2 s is also predicted, again at 5 g/45 ml water.

A knowledge of the equilibrium isotope distribution between chloroform and water is helpful in designing the exchange section of a tritium recovery process. Scharlin has reported equilibrium constant data for deuterium in this system (*24*); at 25°C $K_3 = 1.107$ for reaction (3) in the liquid state. Since $K_4 = 3.76$ (*24*), one can calculate $K_5 = 0.57$. Thus the separation factor $\alpha = 2K = 1.14$, which indicates that the D is favored in chloroform relative to water. This effect is similar to that found for the fluoroform/water system, where $\alpha_{25°C}$ (extrapolated) = 1.29 (*25*).

$$CHCl_3 + \tfrac{1}{2} D_2O \overset{K_3}{\rightleftarrows} CDCl_3 + \tfrac{1}{2} H_2O \quad (3)$$

$$H_2O + D_2O \overset{K_4}{\rightleftarrows} 2HDO \quad (4)$$

$$CHCl_3 + HDO \overset{K_5}{\rightleftarrows} CDCl_3 + H_2O \quad (5)$$

CONCLUSION

Strongly basic ion-exchange resins have been shown to be very active for catalysis of deuterium transfer between liquid chloroform and water under stirred slurry conditions at 25°C. Rate enhancements of ~5–25× were observed for the resin-supported hydroxide ion relative to the two-phase NaOH system. Chloroform solubility in the resin structure is believed to be responsible for the effect.

ACKNOWLEDGMENT

The authors thank Dr. J. H. Rolston for discussions related to the subject of this paper.

REFERENCES

1. Marling, J. B., and Herman, I. P., *J. Chem. Phys.* **72,** 5603 (1980).
2. Bigeleisen, J., Hammond, W. B., and Tuccio, S., *Nucl. Sci. Eng.* **83,** 473 (1983).
3. Evans, D. K., McAlpine, R. D., and Adams, H. M., *J. Chem. Phys.* **77,** 3551 (1982).
4. Sugita, K., Ishikawa, Y., and Aral, S., *J. Phys. Chem.* **87,** 3469 (1983).
5. Moser, J., Morand, P., Duperrex, R., and van den Bergh, H., *Chem. Phys.* **79,** 277 (1983).
6. Symons, E. A., Bonnett, J. D., and de L. Martins, M., *Canad. J. Chem.* **61,** 2627 (1983).
7. Symons, E. A., Clermont, M. J., and Coderre, L. A., *J. Amer. Chem. Soc.* **103,** 3131 (1981).
8. Symons, E. A., and Clermont, M. J., *J. Amer. Chem. Soc.* **103,** 3127 (1981).
9. Hine, J., and Landford, P. B., *J. Amer. Chem. Soc.* **79,** 5497 (1957).
10. Hine, J., and Ehrenson, S. J., *J. Amer. Chem. Soc.* **80,** 824 (1958).
11. Maienschein, J. L., Magnotta, F., Herman, I. P., Aldridge, F. T., and Hsiao, P., *Nucl. Technol./Fusion* **4,** 121 (1983).
12. McAlpine, R. D., Goodale, J. W., and Evans, D. K., submitted for publication.
13. Hine, J., "Physical Organic Chemistry," 2nd ed., p. 487. McGraw–Hill, New York, 1962.
14. Horvath, A. L., "Halogenated Hydrocarbons: Solubility–Miscibility with Water," p. 485. Dekker, New York, 1982.
15. Hine, J., Peek, R. C., Jr., and Oakes, B. D., *J. Amer. Chem. Soc.* **76,** 827 (1954).
16. Symons, E. A., Rolston, J. H., Baldisera, L. A., Drover, J. C. G., and Bonnett, J. D., *Canad. J. Chem.* **61,** 1301 (1983).
17. Hine, J., Burske, N. W., Hine, M., and Langford, P. B., *J. Amer. Chem. Soc.* **79,** 1406 (1957).
18. Hine, J., and Dowell, A. M., Jr., *J. Amer. Chem. Soc.* **76,** 2688 (1954).

19. Kresge, A. J., and Powell, M. F., *Int. J. Chem. Kinet.* **14,** 19 (1982).
20. Margolin, Z., and Long, F. A., *J. Amer. Chem. Soc.* **95,** 2757 (1973).
21. Lin, A. C., Chiang, Y., Dahlberg, D. B., and Kresge, A. J., *J. Amer. Chem. Soc.* **105,** 5380 (1983).
22. Streitwieser, A., Jr., Hollyhead, W. B., Pudjaatmaka, A. H., Owens, P. H., Kruger, T. L., Rubenstein, P. A., MacQuarrie, R. A., Brokaw, M. L., Chu, W. K. C., and Niemeyer, H. M., *J. Amer. Chem. Soc.* **93,** 5088 (1971).
23. Gold, V., and Grist, S., *J. Chem. Soc. Perkin Trans. 1,* 89 (1972).
24. Scharlin, P., *Acta Chem. Scand. Ser. A* **36,** 117 (1982).
25. Symons, E. A., and Bonnett, J. D., *J. Phys. Chem.* **88,** 866 (1984).