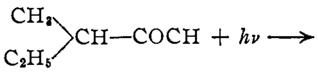
and have suggested that this might be a cyclic rearrangement, though there appeared to be no likely reason for it. Similar results are found for dipropyl ketone.[17]

These surprising but well-established results have been confirmed recently by Nicholson[2] for the ketones CH_3COR where R is *n*-propyl, *n*-butyl, *n*-amyl, isopropyl and *sec*-butyl. In addition to the expected radical decomposition all except the isopropyl compound decomposed by intramolecular processes according to

$$\left.\begin{matrix} C_3H_7COCH_3 \\ C_4H_9COCH_3 \\ C_5H_{11}COCH_3 \end{matrix}\right\} + h\nu \longrightarrow \left\{\begin{matrix} CH_2{=}CH_2 \\ CH_3CH{=}CH_2 \\ C_5H_9CH{=}CH_2 \end{matrix}\right\} + CH_3COCH_3 \quad (4.05)$$

and



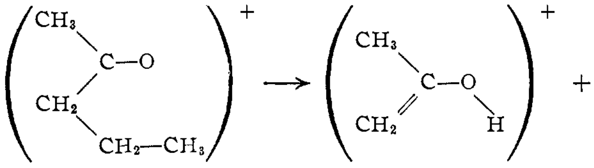
$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!CH{-}COCH + h\nu \longrightarrow CH_2{=}CH_2 + C_2H_5COCH_3 \quad (4.06)$$

These are exact parallels to (4.03).

Nicholson also investigated the electron impact fragmentation patterns at the ionization potential of y_0 and found a close correspondence between the results and (4.05) and (4.06). In all cases the largest peak was at mass 43 (acetyl), and a significant peak occurred at mass 58 except when R was isopropyl or *sec*-butyl. Mass 58 must be formed by rearrangement and was attributed to acetone. No unexpected fragments were observed from methyl isopropyl ketone, while methyl *sec*-butyl ketone gave a peak at mass 72, attributed to methyl ethyl ketone, instead of one at 58. The rearrangements can occur both on photolysis and ionization, though at first it seems surprising that energy absorptions so characteristic of the carbonyl group should produce such profound changes in the region C_1 to C_3.

Light absorption and ionization involve a y_0 electron and both cause a loss of electronic charge from the neighborhood of the oxygen which favors movements of the nuclei giving an increase of electron density near it. In the photolysis the electron is partly removed to the carbonyl carbon and high angular distortions about that atom are favored.

By using atomic models it is seen that hydrogens on C_2, C_3, and C_4 can all approach the oxygen from the lone-pair direction. Since the field near the oxygen is strong it seems likely that the transfer of a hydrogen from C_3 to the oxygen occurs, the transfer being from C_3 because this, when combined with a simultaneous break between C_1 and C_2, gives more stable products than can be formed in any other way. For the methyl propyl ketone ion the result would be



$CH_2{=}CH_2$ (4.07)

with a similar mechanism for the polar state produced by photolysis. The positive charge is expected on the acetone fragment because conjugation in the system CH_2–C–O will delocalize it. Consideration of the symmetries of the orbitals during the rearrangement shows that the olefin will be in the lowest electronic state.

The cyclic rearrangement (4.07) accounts for Nicholson's results in all cases and seems quite reasonable when the effect of the positive charge in the neighborhood of the oxygen is considered.

It is a pleasure to thank Professor F. S. Dainton for much help and encouragement during the course of this work, Dr. E. Collinson for a useful discussion, and the Salters' Company for the award of a Research Fellowship.

LEEDS 2, ENGLAND

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[17] C. R. Masson, THIS JOURNAL, **74**, 4731 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Nuclear Magnetic Resonance Studies of the Aluminum Fluoride Complexes

BY ROBERT E. CONNICK AND RICHARD E. POULSON

RECEIVED MAY 25, 1957

The nuclear magnetic resonances of F^{19} and Al^{27} were studied in solutions containing sodium fluoride and aluminum nitrate. The complex ions AlF^{++} and AlF_2^+ could be detected through their separate fluorine resonances and the measured concentrations agreed well with those calculated from the stability constants reported by Brosset and Orring. Only a single resonance was observed in solutions containing the higher complexes. The Al^{27} resonance appeared to be greatly broadened when the aluminum was complexed, presumably because of the coupling of the quadrupole moment with the unsymmetrical electric field. Measurements of the resonance of uncomplexed aluminum ion gave concentrations of Al^{+3} which again agreed well with those predicted from Brosset and Orring's data. From the difference in shielding of F^{19} in AlF^{++} and AlF_2^+ a lower limit was set on the lifetime for exchange of fluorines between these species. Similarly from the width of the aluminum resonance a lower limit could be set on the lifetime for exchange between Al^{+3} and the complexes.

The nuclear magnetic resonance of the fluorine atom is relatively sharp and readily detected. Therefore it is a potentially useful tool in studying the aqueous complexes of fluoride ions with various metal ions. To test the method an investigation was made of the nuclear magnetic resonance of fluorine in solutions containing sodium fluoride and aluminum ions. The complexing in this system has been studied previously by Brosset and Orring[1]

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[1] C. Brosset and J. Orring, *Svensk. Kem. Tid.*, **55**, 101 (1943).

who measured the complexing constants for AlF_n^{+3-n}, where n ran from 1 to 6, at an ionic strength of 0.5 and at 25°. Latimer and Jolly[2] have determined calorimetrically the heats and entropies of these reactions.

In addition to the fluorine resonance the resonance of the aluminum nucleus was measured for some of the solutions. Although this resonance is considerably broader than the fluorine resonance because of the quadrupole moment of the aluminum, these measurements yielded valuable information in the studies.

Experimental

The F^{19} resonance measurements were made with a Varian Model 4300B high resolution nuclear magnetic resonance spectrometer at a frequency of 40 Mc. and a magnetic field of approximately 10^4 gauss. Samples of about 10-ml. volume were contained in 15 × 125 mm. Pyrex test-tubes. The dimensions of the rf pick-up coil were 17 mm. diameter and 1 mm. height. This coil gave approximately six times the signal of the 5 mm. probe insert.

Nuclear magnetic resonance shifts are reported here as $\sigma_r = 10^6 \times (H_c - H_r)/H_r$ where H_c is the magnetic field required for resonance in the compound studied and H_r is the field for resonance in the indicated reference compound. One σ-unit then corresponds to nuclear magnetic shielding of one part per million (p.p.m.) of the applied field. The nuclear magnetic resonance shifts of the fluorine compounds were measured in the following way. A small sawtooth sweep field was calibrated using the separation of the OH and CH_3 bands in ethyl alcohol as a standard. This separation was taken as 4.1 ± 0.1 p.p.m.[3] The calibration was made against distance on a Sanborn Fast-Writing Recorder which was used to record the absorption curves.

After this primary calibration of the sweep field, the steady magnetic field was raised until the fluorine spectrum of a solution which was 2 M in aluminum nitrate and 2 M in sodium fluoride could be observed. The position of the more intense peak of this doublet resonance was measured with respect to 47% boron trifluoride dissolved in ether (Coleman, Mathieson and Bell) and this value used henceforth as a secondary standard for field calibration. The reference compound for this and subsequent aluminum fluoride shift measurements was contained in a 2 mm. i.d. glass tube secured vertically in the center of the sample tube. Shift of the resonance position of the reference compound due to variation of diamagnetic susceptibilities of the samples run was found to be negligible for this work. This method allowed a sample-to-sample and day-to-day reproducibility of shift measurements to within ±0.3 p.p.m. Line widths of approximately 0.6 p.p.m. were observed under the best conditions of magnetic field homogeneity encountered during the measurements on the fluorides. The widths, however, were so irreproducible that there were uncertainties of about 30% in them. The applied radiofrequency field was maintained at a level low enough to avoid appreciable saturation effects on the line widths or intensities.

All measurements were made at room temperature. The sample temperature varied from about 25 to 30°.

The Al^{27} measurements were made with a Varian Model V4200A variable frequency nuclear magnetic resonance spectrometer at a frequency of 10.4 Mc and a magnetic field of approximately 9400 gauss. The samples were contained in the same test-tubes as for the fluoride measurements. The derivative of the absorption curve was automatically recorded as the output of a phase sensitive detector. A sinusoidal field modulation of 20 c.p.s. was used.

Materials.—Baker and Adamson reagent grade sodium fluoride and aluminum nitrate were used to prepare the solutions. Stock aluminum nitrate solutions were standardized by gravimetric determination of the aluminum as the 8-hydroxyquinolinol compound. Sodium fluoride was added quantitatively to the solutions either as dry NaF or from a stock solution.

Because of the large effects of paramagnetic ions on resonances the possibility of the presence in the reagents of the most common one, *i.e.*, ferric ion, was checked. Colorimetric tests were run with thiocyanate using appropriate standards and blanks. To test the sodium fluoride solutions excess aluminum nitrate was added to destroy any ferric fluoride complexes which would otherwise prevent the formation of the ferric thiocyanate complex. The tests showed that the maximum amount of ferric present from all of the reagents in any of the experiments was less than one-thirtieth of that amount which broadened only slightly the F^{19} resonances in a 1.8 M $Al(NO_3)_3$ plus 1.8 M NaF solution.

Results and Discussion

Brosset and Orring[1] have measured the complexing quotients for the following reactions at 25° and at an ionic strength of 0.5

$Al^{+3} + F^- = AlF^{+2}$ $Q_1 = 1.35 \times 10^6$
$AlF^{+2} + F^- = AlF_2^+$ $Q_2 = 1.05 \times 10^5$
$AlF_2^+ + F^- = AlF_3$ $Q_3 = 7.1 \times 10^3$
$AlF_3 + F^- = AlF_4^-$ $Q_4 = 5.5 \times 10^2$
$AlF_4^- + F^- = AlF_5^{--}$ $Q_5 = 43$
$AlF_5^{--} + F^- = AlF_6^{-3}$ $Q_6 = 3$

The Q's are expressed in concentrations of the appropriate species, *e.g.*, $Q_1 = (AlF^{+2})(Al^{+3})^{-1}\cdot(F^-)^{-1}$ with parentheses indicating moles per liter, M. It is clear that these complexes are very stable and that the concentration of free fluoride ion is extremely small when the total aluminum and fluoride concentrations are comparable. Thus solutions of all but the highest complexes can be prepared in which a negligible fraction of the fluoride is free.

An additional equilibrium to be considered is the ionization of HF[4]

$$HF = H^+ + F^- \quad K = 6.71 \times 10^{-4}$$

In most of the experiments reported here the hydrogen ion concentration was low and the HF concentration therefore negligible.

Position of Fluorine Resonance for Various F–Al Ratios.—The fluorine resonance position was measured for a series of solutions containing sodium fluoride and aluminum nitrate in varying ratios. The data are presented in Table I. In the third column is given the fluorine chemical shift relative to the boron trifluoride–ether standard, σ_B. With the first solution the maxima of two partially overlapping resonances were observed at the positions indicated. In all other solutions only a single resonance was seen. Estimates from the complexing quotients for an ionic strength of 0.5 indicate that the principal species in each of these solutions is the complex with the number of fluorides per aluminum corresponding to the ratio of stoichiometric fluoride to aluminum, although there are appreciable amounts of the next lower and higher complexes present also.

The presence of two resonances in the first solution indicates the existence of two non-equivalent fluorides. As discussed below, the peaks can be identified with AlF^{++} and AlF_2^+ at σ_B of 3.6 and 3.1 p.p.m., respectively. The appearance of only a single resonance at F/Al ratios of 2 and higher cannot be interpreted unambiguously. There might be more than a single resonance, corresponding to the various species in each solution, but with intensities

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[2] W. M. Latimer and W. L. Jolly, THIS JOURNAL, **75**, 1548 (1953).

[3] J. T. Arnold, *Phys. Revs.*, **102**, 146 (1956).

[4] H. Broene and T. DeVries, THIS JOURNAL, **69**, 1644 (1947).

TABLE I

FLUORINE RESONANCES IN SOLUTIONS WITH VARYING SODIUM FLUORIDE TO ALUMINUM NITRATE RATIOS (0.500 *M* NaF)

Moles NAF / Moles $Al(NO_3)_3$	$Al(NO_3)_3$, *M*	σ_B	Apparent width, p.p.m.
1	0.500	3.6	0.6
		3.1	.6
2	.250	3.0	.6
3	.167	2.8	1.0
4	.125	3.0	*ca.* 2
5	.100	3	*ca.* 3

and positions such that the individual peaks cannot be resolved. On the other hand, rapid exchange of the fluoride ions between the various species in these solutions would give rise to a single resonance. The available data did not permit a decision between these possibilities.

The very small difference in the position of the AlF^{++} and AlF_2^+ resonances, *i.e.*, 0.5 p.p.m., as well as the small shifts of the higher fluoride complexes, were quite unexpected. The fluorine resonance shifts 35 p.p.m. toward a higher field strength in going from aqueous fluoride ion to AlF^{++}. Yet the presence of one fluoride on the aluminum ion affects the resonance of a second fluoride by only 0.5 p.p.m. shift in the opposite direction. It must be concluded that the fluorine resonance in the aluminum complexes is relatively insensitive to whether water molecules or additional fluorides are attached to the aluminum. On the basis of Saika and Slichter's[5] theory for fluoride shifts it would be concluded that the fluorine is more covalently bonded in AlF_2^+ than in AlF^{++}, and more covalently bonded in aqueous fluoride ion than in the aluminum fluoride complexes, both of which conclusions seem unlikely. Their theory, which correlates resonances of more covalently bonded fluorine compounds, apparently does not apply to the relatively ionic fluorine in the species studied here.

In the last column of Table I are given approximate values of the line width measured at half intensity. The inhomogeneity of the magnetic field is believed to be responsible only in part for the width of even the sharpest lines. Thus AlF^{++} in a 5 mm. tube and corresponding rf probe insert gave a line width only 15% smaller than with the 15 mm. tubes. The boron trifluoride reference showed a width approximately two-thirds that of the AlF^{++}, with both samples in 5-mm. tubes. The boron trifluoride resonance might have been broadened by iron impurities.

Fluorine Resonance of AlF^{++} and AlF_2.$^+$—Some typical resonance curves for solutions equimolar in sodium fluoride and aluminum nitrate are shown in Fig. 1. It is seen that there is incomplete resolution and that the resolution varies somewhat with the solution composition, as will be discussed elsewhere.

Solutions at varying aluminum nitrate and sodium fluoride concentrations were measured. The results are presented in Table II. The range of concentrations was limited by the low signal intensity at low fluoride concentrations. The positions of the resonances varied somewhat with salt concentration as will be discussed in another paper.

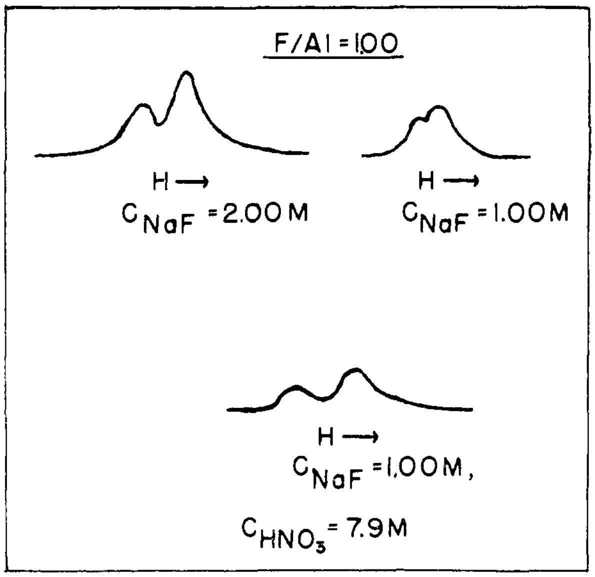

Fig. 1.—Typical F^{19} resonance curves for equal aluminum nitrate and sodium fluoride concentrations.

TABLE II

RELATIVE INTENSITIES OF AlF^{++} AND AlF_2^+ FLUORINE RESONANCES

Al-$(NO_3)_3$, *M*	NaF, *M*	HNO_3, *M*	Intensity of AlF^{++} resonance / Intensity of AlF_2^+ resonance, Obsd.	Intensity of AlF^{++} resonance / Intensity of AlF_2^+ resonance, Calcd.	$3(AlF_3)/2(AlF_2^+)$, Calcd.
2.00	1.00	...	7	7.7	0.007
1.00	0.500	...	10	7.7	.007
1.33	1.00	...	3	3.6	.014
0.667	0.500	...	4	3.6	.014
2.00	2.00	...	1.9[a]	1.8	.03
1.00	1.00	...	2	1.8	.03
1.00	1.00	0.500	1.7[a]	1.8	.03
1.00	1.00	1.60	1.8[a]	1.8	.03
1.00	1.00	4.70	1.8[a]	1.8	.03
1.00	1.00	7.90	1.9[a]	1.8	.03
0.400	0.440	...	1.1	1.4	.04
.800	.98	...	0.9	1.00	.05
.330	.44	...	.5–1	0.78	.06
1.00	1.44	...	.5–1	.57	.09
0.667	0.96	...	.5–1	.57	.09
.286	0.44	...	Single line	.44	.12

[a] Average value from at least four observations at the best field homogeneity obtained in this work and with the resonance lines relatively well resolved.

The observed ratio of intensities in the fourth column were calculated from the relative peak heights, with corrections being made for overlap of the resonances. The assumption is made, therefore, that the shapes of the two curves in a given solution are identical. The calculated ratios in the fifth column were obtained from the equilibrium quotients cited above and are equal to $(AlF^{++})/2\cdot(AlF_2^+)$. It is seen that the agreement is fairly good, especially where the peaks were well resolved. Perfect agreement should not be expected because the calculated values refer only to an ionic strength of 0.5 (principal constituent KNO_3) at 25°

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(5) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

Variations in temperature are probably not important because the heats of complexing are small.[2]

In the sixth column is given the calculated ratio of resonance intensities for the AlF_3 and AlF_2^+ species. No separate resonance corresponding to AlF_3 could be distinguished so that no comparison can be made to observed values.

The agreement between the fourth and fifth columns of Table II is the basis for assigning the two resonances to the species AlF^+ and AlF_2^{++}.

The equilibrium quotient for the reaction

$$Al^{+3} + AlF_2^+ = 2AlF^+ \tag{1}$$

can be calculated from the ratio of the peak heights if the highly plausible assumption is made that aluminum and fluorine are present in significant amounts only as these three species. Values are not given because the data are not accurate and because, within the accuracy of the measurements, the equilibrium quotient does not differ from that for an ionic strength of 0.5, as is evident from columns 4 and 5 of Table II.

Aluminum Resonance.—The amplitude of the aluminum nuclear magnetic resonance was measured for a number of solutions containing aluminum nitrate and sodium fluoride. The results are given in Table III. The resonance width appeared to be the same for all solutions and approximately 4 p.p.m. The position of the resonance did not change noticeably; the resonance for 2 *M* $Al(NO_3)_3$ plus 2 *M* NaF checked with that of 2 *M* $Al(NO_3)_3$ within one p.p.m.

TABLE III

ALUMINUM RESONANCE IN SOLUTIONS OF SODIUM FLUORIDE AND ALUMINUM NITRATE

$Al(NO_3)_3$, *M*	NaF, *M*	$(Al^{+3})_{exptl}$, *M*	$\frac{(Al^{+3})_{exptl}}{(Al^{+3})_{calcd}}$
1.33	1.00	0.33	0.75
1.00	1.00	.22	1.2
0.80	0.98	.09	1.2
.67	.96	.03	1.0
.57	.95	.01	1
2.00	2.00	.37	1.0
0.70	0.70	.14	1.1
.50	.50	.10	1.1
.300	.300	.05	0.9

The observed signal amplitude was approximately proportional to the values listed in the third column of Table III. It is seen that these values decrease much more rapidly in the first five experiments than does the stoichiometric aluminum concentration. Since the proportion of aluminum fluoride complexes is increasing, it must be concluded that the resonance of the complexed aluminum species is either greatly broadened or occurs at some other frequency. A search from 8 to 13 Mc. failed to reveal any other resonances besides the sodium resonance. It seems safe to conclude that the resonance of aluminum in the complexes is indeed greatly broadened. Such an effect would be expected because the large quadrupole moment of the aluminum should lead to coupling and short relaxation times in the unsymmetrical field of the complexes. The sharpness of the resonance of aqueous aluminum ion indicates a highly symmetrical field and is excellent evidence for 6-fold coördination by water molecules, as expected from crystal structures of aluminum salts.

Assuming then that the observed intensity of the resonance arose only from uncomplexed Al^{+3}, the data were used to calculate the values in the third column, $(Al^{+3})_{exptl}$. First, the amplitude of the absorption derivative in solutions of 0.01 to 2.0 *M* aluminum nitrate was measured and found to be almost linearly proportional to the aluminum ion concentration. Concentrations of Al^{+++} in solutions of aluminum nitrate and sodium fluoride were estimated by interpolation of a calibration curve prepared from data obtained for the aluminum nitrate solutions of known concentration. The reproducibility of the absorption amplitudes in duplicate runs was within *ca.* ± 10%.

In the fourth column of Table III comparison is made between $(Al^{+3})_{exptl}$ and the concentration of aluminum ion calculated from Brosset and Orring's equilibrium quotients, *i.e.*, $(Al^{+3})_{calcd}$. The approximate agreement at the higher salt concentrations indicates a relatively small effect of ionic strength on the equilibrium quotients, as was also evident from the fluorine resonances.

To check that the aluminum resonance intensity was essentially independent of the sodium and nitrate ion concentrations, a 1 *M* $Al(NO_3)_3$ solution was compared to a 1 *M* $Al(NO_3)_3$ plus 3 *M* $NaNO_3$ solution. The maximum in the resonance of the latter was 10% lower than that of the former, perhaps because of viscosity broadening.

Using $(Al^{+3})_{exptl}$ and the plausible assumption that Al^{+3}, AlF^{+2} and AlF_2^+ are the only important aluminum and fluorine containing species in the experiments of Table III, it is possible to calculate the concentrations of these species and the equilibrium quotient of eq. 1. Again the calculation is not reported because the accuracy is not high and because the values would agree within experimental accuracy with those of Brosset and Orring, as shown by the entries of the last column of Table III.

The broadening of the aluminum resonance in aluminum complexes should occur in other systems. The measurement of the concentration of uncomplexed aluminum ion by the above method should, in principle, provide a simple means of measuring complexing constants for such systems providing exchange is slow.

Rates of Exchange.—Since separate resonances were observed for AlF^{++} and AlF_2^+ in the same solution, the exchange of fluoride ions between these species must be slow compared to the reciprocal of the difference in angular precession frequencies of the fluorine nuclei.[6,7] For equal concentrations of fluorines in the two species a lower limit for the lifetime for exchange τ_e can be written as

$$\tau_e > \frac{1}{\Delta\omega} = \frac{10^6}{2\pi\nu\Delta\sigma}$$

where $\Delta\omega$ is the difference in angular precession frequencies, ν is the resonance frequency, and $\Delta\sigma$ is the difference in chemical shifts of the two species. For a 1 *M* $Al(NO_3)_3$ plus 1 *M* NaF solution a lower limit of 0.008 second can be set for τ_e.

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(6) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

(7) P. W. Anderson, *J. Phys. Soc. Japan*, **9**, 317 (1954).

A solution was investigated to determine whether exchange with HF could be detected. It contained 0.100 M $Al(NO_3)_3$, 0.350 M NaF and 1.10 M HNO_3. From Brosset and Orring's equilibrium quotients one calculates that the solution should have contained fluorine atoms distributed roughly as follows: 1 as HF, 1.3 as AlF_3 and 1 as AlF_2^+. Only a single broad resonance was observed at $\sigma_B = 3.3$ whereas a blank with aluminum nitrate omitted gave $\sigma_B = 11$ for HF. Either the estimated HF concentration is much too high or the HF resonance is greatly broadened and not observed, since the position of the resonance does not at all correspond to the calculated weighted average of the resonances of HF and the aluminum fluoride complexes. If the latter case holds, the exchange time of fluoride ion between the complexes and HF must be greater than 5×10^{-4} second.

If it is assumed that the relaxation time T_1 for the aluminum in the aluminum fluoride complexes is much shorter than for aluminum ion, a lower limit to the exchange time for aluminum may be set from the half-width of the resonance. This value is, of course, also a lower limit for T_1 of aluminum ion. It is approximately 0.004 second for the solutions of Table III.

Additional information on rates comes from the work of Brosset and Orring[1] who reported measurable slowness in the formation of AlF^{++} in solutions containing aluminum, ferric and fluoride ions at roughly 10^{-3} M concentrations. It may be concluded that under these conditions the net transfer of a fluoride ion from a ferric ion to an aluminum ion is slow, the reaction requiring an hour to approach completion. Assuming that the fluoride was added last in their experiment it may also be concluded that fluoride ion reacts very rapidly with ferric ion, and more rapidly than with aluminum ion.

Acknowledgment.—The authors are indebted to Dr. Power Sogo for his generous guidance in the experimental work and to Dr. Bruce R. McGarvey for valuable discussions. This work was performed under the auspices of the U. S. Atomic Energy Commission.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

Isotopic Exchange Reactions between Phosphorus Trichloride and Phosphorus Pentachloride[1]

BY WARREN E. BECKER AND ROWLAND E. JOHNSON[2]

RECEIVED MAY 10, 1957

A measurable exchange of isotopically labeled phosphorus and chlorine has been observed between phosphorus trichloride and phosphorus pentachloride in carbon tetrachloride solution. The exchange rates are the same within experimental error and the reaction is first order in phosphorus pentachloride and zero order in phosphorus trichloride. The reactions were studied over a temperature range from 0.1 to 50.0° and the activation energy has been determined. The catalytic effect of hydrogen chloride on the chlorine exchange was investigated.

Introduction

It has been shown[3] that a dimeric compound of antimony pentachloride exists, and represents an important path for the exchange of antimony between the trichloride and pentachloride. In the line of a general examination of the isotopic exchange reactions of the Group V halides, we have measured the kinetics of the exchanges of phosphorus and chlorine between phosphorus trichloride and phosphorus pentachloride. We find no evidence for a corresponding complex in the phosphorus system and the exchanges proceed *via* a simple dissociative mechanism.

Experimental

Materials.—Phosphorus trichloride, phosphorus pentachloride, chlorine, carbon tetrachloride and hydrogen chloride were treated as described previously.[4]

Phosphorus trichloride-P^{32} was prepared from red phosphorus which had been neutron irradiated at the Oak Ridge National Laboratory. Chlorine of normal isotopic ratio was added to the phosphorus suspended in boiling phosphorus trichloride.[5] The product mixture was purified as described previously and sealed in small ampules until used. The activity of a sample decayed with a half time of 14.5 days, observed for P^{32} is 14.3 days.[6] This latter figure was used to correct for radioactive decay.

Phosphorus trichloride-Cl^{36} was prepared from red phosphorus of normal isotopic ratio and chlorine-Cl^{36}. Hydrogen chloride-Cl^{36}, received on allocation from the Atomic Energy Commission, was converted to silver chloride-Cl^{36}. This was exchanged at 450° in a sealed Pyrex bulb with a large excess of chlorine gas. The labeled chlorine was removed and allowed to react with a slight excess of red phosphorus in a sealed Pyrex bulb at about 100°. The product was diluted with inactive phosphorus trichloride and purified and stored as described above.

Separate solutions of the reactants (phosphorus trichloride-P^{32} and phosphorus pentachloride in one series of runs, phosphorus trichloride-Cl^{36} and phosphorus pentachloride in another series) in carbon tetrachloride were prepared inside a dry box by breaking the appropriate ampules in the solvent and diluting to a known volume. Recovery of the glass of the ampule and weighing allowed us to calculate the solution concentrations. As a check, aliquots of the

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[1] Work performed on Contract No. AT-(40-1)-1317 with the Atomic Energy Commission. Presented in part before the Inorganic Division of the American Chemical Society in Miami, April, 1957. Presented in partial fulfillment of the requirements of the degree of Doctor of Philosophy by Warren E. Becker, complete dissertation to be filed in the Library, Florida State University.

[2] Texas Instruments, Inc., Dallas, Texas.

[3] (a) F. B. Barker and M. Kahn, THIS JOURNAL, **78**, 1317 (1956); (b) V. Gutmann, *Monatsh.*, **82**, 473 (1951).

[4] J. J. Downs and R. E. Johnson, THIS JOURNAL, **77**, 2098 (1955).

[5] "Inorganic Syntheses," W. C. Fernelius, Ed., Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 145.

[6] J. M. Hollander, I. Perlman and G. T. Seaborg, *Rev. Mod. Phys.*, **25**, 469 (1953).