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Kinetics of Isotope-Exchange Reactions of Fluorine with Some Halogen Fluorides*

RICHARD M. ADAMS,† RICHARD B. BERNSTEIN,‡ AND JOSEPH J. KATZ
Chemistry Division, Argonne National Laboratory, Lemont, Illinois

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Quantitative kinetic data on the isotope-exchange reaction of fluorine with chlorine trifluoride, bromine pentafluoride, and iodine heptafluoride have been obtained using F^{18} ($t_{\frac{1}{2}}=112$ min) tracer. The materials were handled in a metal vacuum line, and the exchanges were carried out in a 2-liter nickel reaction vessel at three temperatures in the range 181–257°C. While the experimental data do not uniquely determine the mechanism, they strongly suggest that exchange takes place either through a heterogeneous catalysis by the metal fluoride coating on the walls of the reaction vessel, or by a combination of the heterogeneous mechanism plus a homogeneous gas-phase exchange in those cases where a measurable amount of dissociation of the halogen fluoride occurs at the temperature of exchange. It has been shown to be unlikely that the observed exchanges take place through either an atomic mechanism or a purely homogeneous mechanism. It has also been shown that all fluorine atoms in the halogen fluoride molecules are exchangeable.

I. INTRODUCTION

THE radioactive nuclide F^{18} has been used in three previous investigations of the exchangeability of fluorine between various fluorine-containing molecules.

Dodgen and Libby[1] found a measurable amount of exchange at about 200°C between fluorine and hydrogen fluoride; the reaction was postulated to occur primarily through heterogeneous catalysis. Rogers and Katz[2] employed F^{18} to study the exchange between hydrogen fluoride and some halogen fluorides. Exchange was found to be practically instantaneous at room temperature in the gas phase, and it was postulated that reaction took place via a homogeneous mechanism involving the formation of relatively stable molecular complexes.

Recently a qualitative investigation of the gas-phase exchange between some halogen fluorides and elemental fluorine has been carried out by Bernstein and Katz.[3] The results indicated that there was no exchange below about 100°C, but that measurable rates of exchange occurred above 200°C.

The present study was undertaken to obtain quantitative kinetic data leading to the elucidation of the mechanisms of the fluorine-halogen fluoride exchanges.

II. MATERIALS AND APPARATUS

Anhydrous chlorine trifluoride and bromine pentafluoride were obtained from Harshaw Chemical Company. Iodine heptafluoride was prepared by the method of Schumb and Lynch.[4] The compounds were purified before use, and vapor pressures and molecular weight determinations (see Table I) were used to establish their purity. Fluorine (Pennsylvania Salt Company) was used directly from the tank. Analysis showed a fluorine content of 93.5±1.0 percent. Mass spectrometric analysis indicated that the inert residual 6.5-percent impurity was essentially air. Certain check experiments were run with another cylinder of fluorine of 100±1 percent purity in order to determine that the air had no effect on the results.

Lithium fluoride (used in the preparation of samples for irradiation to produce F^{18} activity) was Baker's Analyzed Reagent Grade, with a chloride impurity of 0.002 percent. Aluminum oxide used in the preparation of these samples was Linde, synthetic gem quality, Type A-5175, with a maximum chloride impurity of 0.002 percent. It is important that the chloride impurity in these compounds be as low as possible, because an interfering Cl^{38} activity is produced by neutron irradiation.

The 112-minute nuclide F^{18} was prepared by the nuclear reaction[5] $O^{16}(t,n)F^{18}$ by irradiating a mixture of Al_2O_3 and LiF with thermal neutrons in a nuclear pile.[3] The usual procedure was to irradiate about 1.5 grams of an equimolar mixture for 7 hours and allow 4 hours cooling time before the first count. This ratio of

TABLE I. Physical properties of halogen fluorides.

	Vapor pressure (mm)			Molecular weight	
XF_n	Obs	Calc	t°C	Obs	Calc
ClF_3	47	47.5[a]	−40	92.21	92.46
IF_7	600	617[b]	0	260.7	259.9
BrF_5	370	375[c]	23	···	174.9

[a] Grisard, Bernhardt, and Oliver, J. Am. Chem. Soc. **73**, 5725 (1951).
[b] O. Ruff and R. Keim, Z. anorg. u. allgem. Chem. **193**, 176 (1930).
[c] O. Ruff and W. Menzel, Z. anorg. u. allgem. Chem. **202**, 49 (1931).

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‡ Department of Chemistry, Illinois Institute of Technology, Participating Institution Program. Present address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

[1] H. W. Dodgen and W. F. Libby, J. Chem. Phys. **17**, 951 (1949).

[2] M. T. Rogers and J. J. Katz, J. Am. Chem. Soc. **74**, 1375 (1952).

[3] R. B. Bernstein and J. J. Katz, J. Phys. Chem. **56**, 885 (1952).

[4] W. C. Schumb and M. A. Lynch, Ind. Eng. Chem. **42**, 1383 (1950).

[5] Knight, Novey, Cannon, and Turkevich, *National Nuclear Energy Series* (McGraw-Hill Book Company, Inc., New York, 1951), Div. IV, Vol. 9, Book 3, Paper 326.

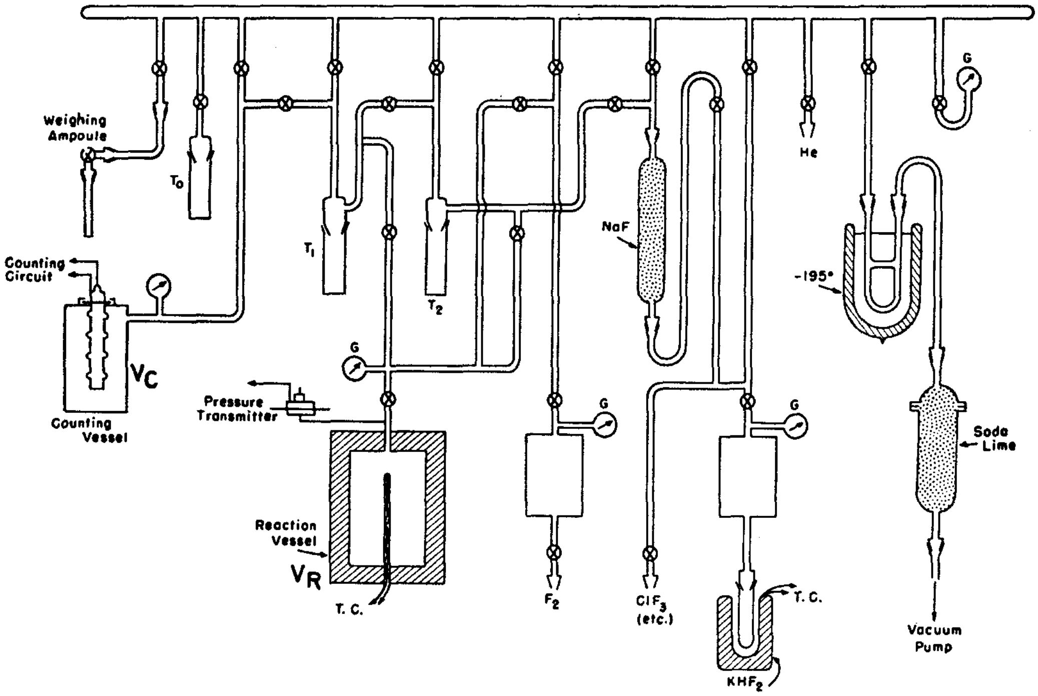

FIG. 1. Apparatus for studying fluorine exchange reactions.

irradiation to cooling time was adopted in order to minimize the Cl^{38} activity ($t_{\frac{1}{2}}=38$ min) and to maximize the F^{18} activity. By this procedure it was possible to produce at least 5000 counts/min of F^{18} activity at the time of initial counting, with less than 1 percent contamination from the Cl^{38} activity. The radiochemical purity of the activity was determined by following the decay of F^{18}, which gave a half-life of 112 ± 1 minutes, over a period of 4 to 5 half-lives (twice the length of an average experiment). A negligible amount of a long-lived activity with approximately a 30-hour half-life (probably a mixture of Br^{80} and Br^{82}) was observed to be present also.

F^{18} was counted as elemental gaseous fluorine or as the appropriate gaseous halogen fluoride in a 350-ml nickel vessel using a Victoreen 1B85 aluminum Thyrode as a counting tube. A vacuum-tight seal was made between the counting tube and the nickel vessel with a Fluorothene gasket and a compression screw. The solder joint of the Thyrode was protected by Fluorothene wax and, when properly prepared, the tube could be used for 3 or 4 months before failure occurred because of corrosion at the solder joint. A Nuclear Instrument and Chemical Company Scaler, Model 165, was used for counting.

The exchange experiments were all conducted in a vacuum line (see Fig. 1) constructed of copper and nickel with silver-soldered and flared connections. Cold traps T_0, T_1, and T_2 were machined from $\frac{3}{4}$-inch Fluorothene rod. Helicoid gauges equipped with Monel-metal Bourdon tubes were used to read rough pressures. Precise pressure measurements were made using a Booth-Cromer[6] nickel diaphragm null-type pressure transmitter with an external pressure balancing system.

The 2184-ml reaction vessel *VR* was made of nickel with all joints nickel-welded. It was heated electrically and completely insulated with asbestos. Temperature variation along the length of the vessel, observed by means of thermocouples at each end and one in a central thermocouple well, was less than 0.5°C. The temperature in any given experiment was constant to ±0.5°C. A duplicate of this vessel, with a removable gasketed cap on one end through which additional material could be added, was used in certain experiments in which surface effects were studied.

III. EXCHANGE PROCEDURE AND ERRORS

A description of a typical exchange experiment follows. A sample of irradiated $LiF-Al_2O_3$ is placed in Fluorothene trap T_0 and evacuated. The proper amount of purified halogen fluoride, XF_n, is frozen on to the $LiF-Al_2O_3$ mixture and allowed to warm to room temperature under its own vapor pressure. After the solid-liquid exchange is complete (10 to 20 minutes), the $XF_n{}^*$ is removed and further purified if necessary. It is then expanded into the counting vessel *VC*, and the decay of F^{18} is followed for about $\frac{1}{2}$ hour. The $XF_n{}^*$ is transferred to the reaction vessel *VR*, which is at equilibrium at the temperature chosen for reaction, and the desired quantity of F_2 is introduced by expansion from a tank. After a suitable exchange time at a constant temperature, the mixture of gases is separated quanti-

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[6] S. Cromer, U. S. Atomic Energy Commission Declassified Document MDDC-803, June, 1944.

tatively by expansion into the evacuated counting vessel through traps T_2 and T_1 immersed in liquid nitrogen baths to remove the halogen fluoride. The activity of the F_2^* fraction is determined, after which it is discarded. The XF_n^* fraction is then introduced into the counting vessel and its activity determined.

The total inventory of F^{18} was usually better than 95 percent, and the small losses were shown to be due primarily to exchange with the metal fluoride coating. The gas-phase exchange was calculated by means of the recoverable total activity, i.e., the sum of the F_2^* and XF_n^* activities after exchange.

Assignment of an over-all error to the rate measurements is difficult. Nevertheless, from an estimate of determinate errors, and from a comparison of the results of duplicate experiments, it is believed that those rates obtained in experiments with a contact time greater than 10 minutes are reliable to better than ±10 percent; those rates obtained with contact times of 10 minutes or less are probably reliable to better than ±20 percent.

IV. CALCULATIONS

Using the method of McKay,[7] the rate of exchange has been shown[3] to be

$$R=\frac{2.303}{t}\left(\frac{2nab}{na+2b}\right)\log\left(\frac{1}{1-f}\right), \tag{1}$$

TABLE II. ClF_3-F_2 exchange data at 467°K.

Exp.	Temp. (°K)	Time (min)	ClF_3 ($\times 10^3$)	F_2[b] ($\times 10^3$)	Percent exchange	R[c] ($\times 10^5$)
A. Experiments at constant F_2 concentration.[a] $F_2=8.31\pm0.08\times10^{-3}$.						
41	467	37	0.35	8.12	76.9	3.93
36	467	60	0.85	8.48	71.9	4.70
39	467	60	0.85	8.35	78.3	5.65
37	467	32	0.84	8.19	59.6	6.20
34	468	66	1.27	8.36	67.7	5.32
40	467	60	1.73	8.35	52.8	4.96
23	467	60	2.58	8.40	37.3	4.12
26	468	60	4.11	8.31	27.2	3.75
27	468	70	7.37	8.20	22.3	3.40
43	467	69	9.29	8.32	18.3	3.05
29	468	67	11.90	8.26	14.0	2.54
24	467	60	15.76	8.43	12.7	2.81
B. Experiments at constant ClF_3 concentration. $ClF_3=7.41\pm0.03\times10^{-3}$.						
27	468	70	7.37	8.20	22.3	3.40
2	464	35	7.43	11.70	12.5	4.36
30	468	60	7.40	18.13	22.9	5.96
31	468	70	7.42	18.13	24.7	5.58
32	468	72	7.45	27.34	28.6	7.44
33	467	65	7.36	36.20	32.4	10.19

[a] All concentrations given in this paper are in moles $liter^{-1}$.

[b] All fluorine concentrations have been corrected by the purity factor of the fluorine used.

[c] Units of R throughout this paper are moles $liter^{-1}\ min^{-1}$.

TABLE III. ClF_3-F_2 exchange data at 497°K.

Exp.	Temp. (°K)	Time (min)	ClF_3 ($\times 10^3$)	F_2 ($\times 10^3$)	Percent exchange	R ($\times 10^4$)
A. Experiments at constant F_2 concentration. $F_2=8.87\pm0.14\times10^{-3}$.						
35	497	20	0.61	9.02	86.0	1.63
38	498	20	0.61	8.91	88.9	1.83
22	497	20	0.91	8.97	85.1	2.25
13	497	32	2.01	8.75	82.5	2.44
16	498	32	2.47	8.81	76.2	2.34
15	498	32	3.08	8.74	67.3	2.11
12	497	30	4.07	8.85	62.2	2.34
17	497	32	4.88	8.88	53.5	1.92
10	495	31	7.68	8.96	42.9	1.82
11	498	31	10.81	8.74	34.9	1.57
128	496	60	10.91	8.45	51.2	1.41[a]
127	497	30	10.94	8.53	33.0	1.58[a]
14	496	34	15.45	9.39	29.4	1.31[a]
9	497	33	16.23	8.61	35.3	1.77
8	496	42	16.58	8.72	37.0	1.42
129	496	30	38.35	8.43	28.5	1.67[a]
B. Experiments at constant ClF_3 concentration. $ClF_3=3.13\pm0.03\times10^{-3}$.						
21	498	52	3.16	2.84	71.3	0.86
15	498	32	3.08	8.74	67.3	2.11
19	497	32	3.14	9.71	66.9	2.19
18	497	32	3.16	16.58	80.6	3.78
20	498	22	3.11	26.28	78.7	5.57

[a] R values corrected to $F_2=8.87\times10^{-3}$ using a smooth curve drawn through the fluorine-dependence data given in Part B of this table.

where R = exchange rate; t = contact time; f = fraction exchanged in time t; n = subscript in XF_n; a = moles/liter of XF_n in reaction vessel; and b = moles/liter of F_2 in reaction vessel.

Concentrations of BrF_5 and F_2 have been calculated from observed temperatures and pressures by means of the ideal gas law, which was demonstrated experimentally to be obeyed by these gases. In the case of ClF_3 and IF_7, small corrections have been applied where necessary to the primary data to take into account known facts about their behavior. The data of Schmitz and Schumacher[8] were used to calculate dissociation and association corrections for ClF_3. The data of Bernstein and Katz[3] were used to calculate dissociation corrections for IF_7.

The fraction exchanged was calculated from the relationship $f=G/\beta$, where G is the fraction of the total activity in the fluorine gas, and β is the atomic fraction of fluorine in the form of elemental fluorine in the mixture. The use of this relationship assumes that all the fluorine atoms in the halogen fluoride molecules are exchangeable. This was proved experimentally to be true for all three halogen fluorides used.[9]

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[7] H. A. C. McKay, Nature **142**, 997 (1938).

[8] H. Schmitz and H. J. Schumacher, Z. Naturforsch. **2A**, 362 (1947).

[9] Assume an equimolar mixture of F_2 and ClF_3 in which F^{18} is present initially (in small concentration) only in the ClF_3. If all three fluorine atoms in ClF_3 are exchangeable, then after complete exchange, the probability that the F_2 now contains F^{18} is 2/5, and the probability that the ClF_3 now contains F^{18} is 3/5. Thus, $G=2/5$; and since $\beta=2/5$, then $f=1$. If, however, only two of the

TABLE IV. ClF_3-F_2 exchange data at 530°K.

Exp.	Temp. (°K)	Time (min)	ClF_3 ($\times10^3$)	F_2 ($\times10^3$)	Percent exchange	R ($\times10^4$)
A. Experiments at constant F_2 concentration. $F_2=6.99\pm0.11\times10^{-3}$.						
47	533	8.0	0.58	6.97	89.8	4.39
48	530	8.0	0.74	7.15	92.6	6.26
46	529	11	1.43	6.89	95.3	9.09
45	532	11	2.34	5.31[a]	87.0	9.45[a]
44	529	11	5.25	7.10	74.7	9.34
49	528	10	14.19	6.83	57.2	8.78
B. Experiments at constant ClF_3 concentration. $ClF_3=5.25\times10^{-3}$.						
45	532	11	2.34[b]	5.31	87.0	7.87
44	529	11	5.25	7.10	74.7	9.34
50	527	10	5.23	29.39	91.6	30.70

[a] R value for this run corrected to $F_2=6.99\times10^{-3}$ using a smooth curve drawn through the data in Part B of this table.

[b] This run included here because R changes by only about 1 percent from $ClF_3=2.34\times10^{-3}$ to 5.25×10^{-3} (see Fig. 2).

V. RESULTS AND DISCUSSION

The results of the kinetic studies of the exchanges are given in Tables II through X and in Figs. 2 through 7. The dependence of the rate on the XF_n concentration shows a maximum at all three temperatures in the BrF_5-F_2 exchange, with the maximum becoming less pronounced in the ClF_3-F_2 and IF_7-F_2 exchanges until it almost disappears in the latter. The dependence of the rate on the F_2 concentration is linear for all the exchanges, but it is to be noted that there is a nonzero intercept in the case of the ClF_3-F_2 and IF_7-F_2 exchanges.

Since it is known that ClF_3 and IF_7 dissociate, it is reasonable to suppose that a dissociative mechanism is partly responsible for the exchange observed in these cases. Thus, in the case of ClF_3, dissociation and recombination as in

$$ClF_3^* \xrightarrow{k_1} ClF + F_2^*, \tag{1a}$$

$$ClF + F_2 \xrightarrow{k_{-1}} ClF_3 \tag{1b}$$

will result in exchange. Moreover, the experimental data reveal that there is some similarity between the ClF_3-F_2 and the IF_7-F_2 exchanges, and that these are different from the BrF_5-F_2 exchange. However, the dissociative mechanism alone cannot account for the entire amount of exchange observed, for if it is assumed that the rate-determining step is (1a), i.e., $k_1 \ll k_{-1}$, then the rate of the exchange would be independent of the (F_2) and linearly dependent on (ClF_3), which is contrary to the experimental facts.

TABLE V. IF_7-F_2 exchange data at 454°K.

Exp.	Temp. (°K)	Time (min)	IF_7 ($\times10^3$)	F_2 ($\times10^3$)	Percent exchange	R ($\times10^4$)
A. Experiments at constant F_2 concentration. $F_2=13.88\pm0.11\times10^{-3}$.						
108	454	71	3.33	13.82	36.2	0.82
107	454	66	7.25	13.77	31.5	1.02
109	454	74	11.38	14.04	31.6	1.07
B. Experiments at constant IF_7 concentration. $IF_7=7.28\pm0.03\times10^{-3}$.						
107	454	66	7.25	13.77	31.5	1.02
110	454	61	7.30	31.21	28.7	1.56

The maximum in the graphs of the rate *vs* XF_n concentration suggests that the mechanism is complex, and that some part of the exchange may be heterogeneous, being surface-catalyzed by the metal fluoride coating always present on the surface of the reaction vessel. Let it be assumed that exchange takes place either by a heterogeneous path or by a combination of a heterogeneous plus a homogeneous path, i.e., that the total rate is the sum of the components

$$R_{\text{tot}} = R_{\text{het}} + R_{\text{hom}}. \tag{2}$$

TABLE VI. IF_7-F_2 exchange data at 467°K.

Exp.	Temp. (°K)	Time (min)	IF_7 ($\times10^3$)	F_2 ($\times10^3$)	Percent exchange	R ($\times10^4$)
A. Experiments at constant F_2 concentration. $F_2=14.89\pm0.28\times10^{-3}$.						
94	469	61	1.40	14.84	80.9	1.95
93	468	61	3.28	14.64	65.7	2.25
91	467	61	3.86	15.11	51.3	1.68
86	467	61	6.78	15.16	56.7	2.53
92	468	56	13.10	14.35	56.3	3.34
95	467	62	19.78	15.21	67.2	4.49
B. Experiments at constant IF_7 concentration. $IF_7=3.73\pm0.21\times10^{-3}$.						
98	468	61	3.67	3.15	78.7	1.29
96	467	61	3.91	6.26	56.9	1.19
93	468	61	3.28	14.64	65.7	2.25
91	467	61	3.86	15.11	51.3	1.68
97	467	61	3.94	28.94	61.3	2.91

If the heterogeneous exchange takes place by the competitive adsorption mechanism (the Langmuir[10]-Hinshelwood[11] type), and the homogeneous exchange occurs via the dissociative mechanism, the total rate becomes

$$R_{\text{tot}} = \frac{k_2 x(F_2) y(XF_n)}{[1 + x(F_2) + y(XF_n)]^2} + k_1(XF_n), \tag{3}$$

where x and y are adsorption coefficients of F_2 and XF_n, respectively, and k_2 is the rate constant for the heterogeneous exchange. This may be simplified if the assumption[12] is made that fluorine is much less strongly adsorbed than the halogen fluorides. Equation (3) may

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three fluorine atoms in ClF_3 are exchangeable in the gas phase, there are two important cases to be considered: Case (a), only two F atoms exchange with the solid mixture to introduce F^{18}, and only two exchange in the gas phase with F_2; Case (b), all three F atoms exchange with the solid, but only two exchange in the gas phase. Case (a) would lead to a calculated 125 percent exchange, whereas (b) would lead to 83.4 percent. Experimentally, exchanges calculated on the basis that all the fluorine atoms were exchangeable were observed to range from 98 to 103 percent.

[10] I. Langmuir, Trans. Faraday Soc. **17**, 621 (1921).

[11] C. N. Hinshelwood, *Kinetics of Chemical Change* (Oxford University Press, New York, 1940), p. 178.

[12] This assumption is justified by the fact that little or no exchange of activity between F_2^* and the metal fluoride coating on the walls was observed (see reference 3).

TABLE VII. IF_7-F_2 exchange data at 497°K.

A. Experiments at constant F_2 concentration. $F_2=8.93\pm0.29\times10^{-3}$.

Exp.	Temp. (°K)	Time (min)	IF_7 ($\times10^3$)	F_2 ($\times10^3$)	Percent exchange	R ($\times10^3$)
100	496	10	3.83	8.97	69.1	1.26
101	497	10	6.13	9.00	72.3	1.62
104	496	8.0	6.66	9.24	61.6	1.59[a]
102	497	8.0	14.00	9.22	84.2	3.59
103	496	4.5	17.42	8.21	66.5	3.52

B. Experiments at constant IF_7 concentration. $IF_7=6.29\pm0.19\times10^{-3}$.

Exp.	Temp. (°K)	Time (min)	IF_7 ($\times10^3$)	F_2 ($\times10^3$)	Percent exchange	R ($\times10^3$)
105	497	11	6.15	4.59	89.7	1.56
101	497	10	6.13	9.00	72.3	1.62
104	496	8.0	6.66	9.24	61.6	1.59
106	495	4.8	6.20	25.01	33.4	1.99

[a] 11.0-mm HF added to exchange mixture (4 percent of the total F_2 pressure).

then be written as

$$R_{\text{tot}}=\frac{k_2x(F_2)y(XF_n)}{[1+y(XF_n)]^2}+k_1(XF_n). \tag{4}$$

Qualitatively, Eq. (4) fits the experimental facts; it correctly predicts the observed behavior of the R *vs* (XF_n) curves, and it correctly predicts the linear dependence of the rate on the fluorine concentration. Furthermore, it is to be expected that the temperature dependence of the homogeneous component should be greater than that of the heterogeneous component, and thus that the graphs of R *vs* (XF_n) may flatten out with increasing temperature as in the case of ClF_3, or may even approach a straight line through the origin when the homogeneous component becomes most important, as in the case of IF_7. This is also consistent with the fact that the dissociation-equilibrium constant for IF_7 increases more rapidly with temperature than that for ClF_3, and therefore the homogeneous contribution to exchange in the case of IF_7 could be greater than in the case of ClF_3. In the case of BrF_5 no homogeneous contribution to exchange is expected (except for the possibility that BrF_5 and F_2 may associate to form BrF_7), since BrF_5 is known[3] to be undissociated even at temperatures as high as 400°C. Therefore, the shape of the R *vs* (BrF_5) curves should remain sensibly constant with increasing temperature.

TABLE VIII. BrF_5-F_2 exchange data at 466°K.

A. Experiments at constant F_2 concentration. $F_2=6.32\pm0.05\times10^{-3}$.

Exp.	Temp. (°K)	Time (min)	BrF_5 ($\times10^3$)	F_2 ($\times10^3$)	Percent exchange	R ($\times10^5$)
82	466	60	0.51	6.25	76.6	5.11
81	467	60	0.87	6.26	62.7	5.29
80	466	60	1.47	6.41	46.0	4.80
79	466	60	2.96	6.33	29.8	4.02
78	466	60	5.52	6.35	20.8	3.38

B. Experiments at constant BrF_5 concentration. $BrF_5=5.51\pm0.02\times10^{-3}$.

Exp.	Temp. (°K)	Time (min)	BrF_5 ($\times10^3$)	F_2 ($\times10^3$)	Percent exchange	R ($\times10^5$)
78	466	60	5.52	6.35	20.8	3.38
84	467	60	5.48	16.39	24.3	6.92
83	466	61	5.54	35.64	33.8	13.49

TABLE IX. BrF_5-F_2 exchange data at 497°K.

A. Experiments at constant F_2 concentration. $F_2=4.62\pm0.11\times10^{-3}$.

Exp.	Temp. (°K)	Time (min)	BrF_5 ($\times10^3$)	F_2 ($\times10^3$)	Percent exchange	R ($\times10^4$)
59	496	15	0.40	4.54	81.4	1.83
57	497	15	0.69	4.54	78.5	2.55
55	497	31	1.25	4.87	83.6	2.22
54	497	31	1.73	4.54	72.2	1.83
51	497	27	4.49	4.54	43.1	1.35
58	496	31	8.45	4.71	39.9	1.27

B. Experiments at constant BrF_5 concentration. $BrF_5=4.48\pm0.01\times10^{-3}$.

Exp.	Temp. (°K)	Time (min)	BrF_5 ($\times10^3$)	F_2 ($\times10^3$)	Percent exchange	R ($\times10^4$)
51	497	27	4.49	4.54	43.1	1.35
52	495	31	4.48	15.46	64.3	4.31
53	497	31	4.46	32.56	78.7	8.29

Many examples of heterogeneous reactions are known in which the rate is found to decrease with increasing concentration of some component, as is here observed for the dependence of the rate on XF_n concentration. In the combination of ethylene and hydrogen on a copper catalyst, Pease[13] found that the rate decreases with increasing concentration of ethylene, but increases approximately linearly with the hydrogen concentration. More recently, a rate expression similar to the heterogeneous component of Eq. (4) has been postulated by J. Weber and K. J. Laidler[14] to explain the heterogeneous NH_3-D_2 exchange. Their work verified

TABLE X. BrF_5-F_2 exchange data at 529°K.

A. Experiments at constant F_2 concentration. $F_2=3.98\pm0.06\times10^{-3}$.

Exp.	Temp. (°K)	Time (min)	BrF_5 ($\times10^3$)	F_2 ($\times10^3$)	Percent exchange	R ($\times10^4$)
65	529	5.0	0.50	3.96	89.5	8.52
74	529	5.0	0.51	4.10	81.4	6.53
67	528	5.0	0.52	3.80	77.8	5.81
64	529	5.0	0.52	3.98	87.7	8.22
63	530	5.5	0.83	3.82	71.2	6.06
75	529	5.0	1.48	4.10[a]	54.1	6.06
77	529	4.8	1.50	3.94	51.4	5.84
61	528	10	1.82	3.99	78.1	6.46
60	528	10	3.48	4.06	67.9	6.30
73	529	10	3.50	3.98	62.7	5.39
70	529	10	3.48	4.02[a]	58.5	4.84
72	529	10	3.50	4.01[a]	57.3	4.68
66	529	10	8.57	3.95	47.3	4.28
71	529	10	8.62	3.99[a]	47.7	4.36

B. Experiments at constant BrF_5 concentration. $BrF_5=3.49\pm0.01\times10^{-3}$.

Exp.	Temp. (°K)	Time (min)	BrF_5 ($\times10^3$)	F_2 ($\times10^3$)	Percent exchange	R ($\times10^4$)
60	528	10	3.48	4.06	67.9	6.30
73	529	10	3.50	3.98	62.7	5.39
70	529	10	3.48	4.02[a]	58.5	4.84
72	529	10	3.50	4.01[a]	57.3	4.68
68	529	6.0	3.48	32.07	85.3	43.75

[a] F_2 of 100 percent purity used.

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[13] R. Pease, J. Am. Chem. Soc. **45**, 1196 (1923).

[14] J. Weber and K. J. Laidler, J. Chem. Phys. **19**, 1089 (1951).

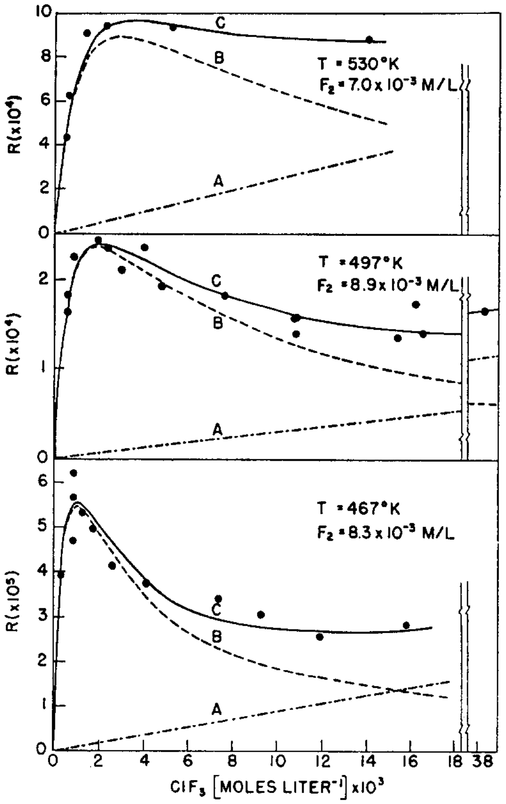

FIG. 2. ClF_3-F_2 exchange. Rate *vs* ClF_3 concentration. A = homogeneous exchange; B = heterogeneous exchange; $C = A + B$; ⊙ = experimental data.

the maximum in the dependence of the rate on the ammonia pressure and, incidentally, is considered evidence for the Langmuir-Hinshelwood type of reaction rather than for the Rideal[15] type.

It should be noted that without the homogeneous term in Eq. (4), the R *vs* (F_2) curves should all extrapolate to the origin at zero fluorine concentration. This is not observed in the IF_7 and ClF_3 exchanges whose rates extrapolate to a nonzero intercept. For the BrF_5 exchange, the rate does extrapolate to zero except for the data at the lowest temperature, where, perhaps, the adsorption term for fluorine in the denominator of Eq. (3) may not be negligible. The lower the temperature the more important this term would be.

TABLE XI. Homogeneous and heterogeneous rate constants.

Exchange	T(°K)	k_1(min^{-1})	(k_2x) (min^{-1})
ClF_3-F_2	467	9.4×10^{-4}	0.027
	497	3.0×10^{-3}	0.11
	530	2.5×10^{-2}	0.51
IF_7-F_2	454	1.6×10^{-3}	0.027
	467	2.0×10^{-2}	0.037
	497	2.1×10^{-1}	0.15
BrF_5-F_2	466	...	0.033
	497	...	0.22
	529	...	0.75

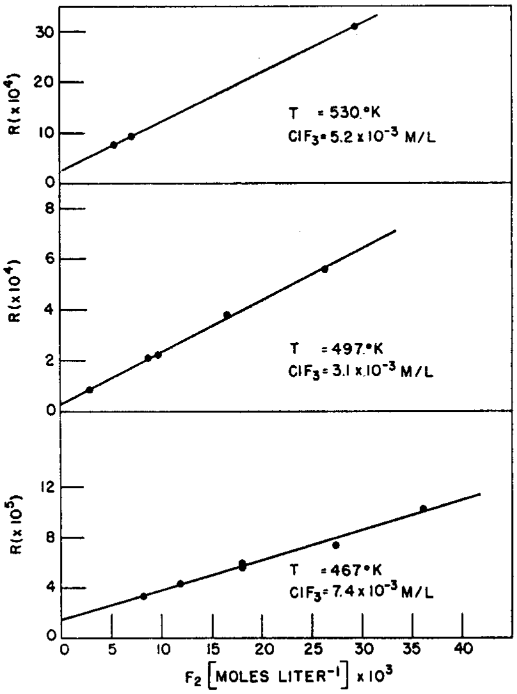

FIG. 3. ClF_3-F_2 exchange. Rate *vs* F_2 concentration.

Since the homogeneous term of Eq. (4) increases linearly with (XF_n), while the heterogeneous term increases to a maximum and then decreases asymptotically to zero, it should be possible at very high XF_n concentrations to find that the rate begins to increase again with increasing (XF_n). An attempt was made to find such behavior in the ClF_3-F_2 exchange at 497°K. Experiment 129 (Table III) was run at a ClF_3 concentration of 38.35×10^{-3} moles liter^{-1}. From Fig. 2 it can be seen that the rate at this concentration is slightly higher than the rate at the flat portion of the curve at lower concentrations. This indicates that the homogeneous contribution to exchange at this temperature may be small enough to be neglected in the region of the maximum. It should then be possible to calculate from the observed data the theoretical curve representing the heterogeneous exchange in the following way. Neglecting the homogeneous term, Eq. (4) may be written

$$R = \frac{Ky(XF_n)}{[1+y(XF_n)]^2}, \tag{5}$$

where

$$K = k_2x(F_2). \tag{6}$$

At the maximum, $(XF_n) = 1/y$, and therefore

$$R_{\max} = 0.25K. \tag{7}$$

Knowing the value of R and the XF_n concentration at

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[15] E. K. Rideal, Proc. Cambridge Phil. Soc. **35**, 130 (1939); Chemistry and Industry **62**, 335 (1943).

the maximum, the value of R at any other concentration may be calculated.

Such a procedure has been followed in calculating the theoretical curves given in Figs. 2 and 4, which show the dependence of the rate on the XF_n concentration in the ClF_3-F_2 and IF_7-F_2 exchanges. It can be seen that the theoretical curves fit the experimental data well. The importance of the homogeneous component increases very rapidly with temperature for the IF_7-F_2 exchange but not for the ClF_3-F_2 exchange. This is probably owing to the fact that the dissociation equilibrium constant for IF_7 increases more sharply with temperature than that for ClF_3.

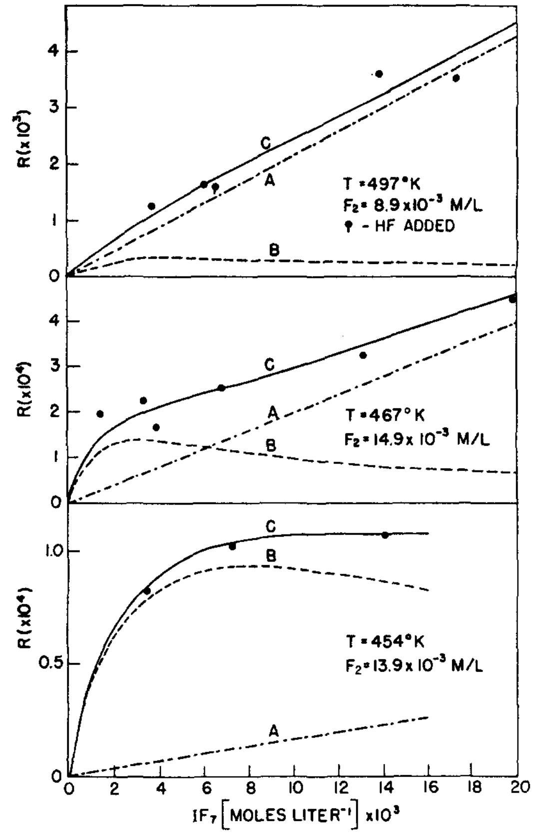

FIG. 4. IF_7-F_2 exchange. Rate *vs* IF_7 concentration. A = homogeneous exchange; B = heterogeneous exchange; $C = A+B$; ⊙ = experimental data.

For the BrF_5-F_2 exchange the theoretical curves given in Fig. 6 represent only the theoretical heterogeneous exchange. The experimental data are represented fairly well on the assumption that all of the exchange is heterogeneous, except at the higher concentrations of BrF_5. The fact that the experimental data all fall above the theoretical curves at high (BrF_5) might indicate that there also exists some homogeneous component to this exchange. A small contribution to exchange of the bimolecular association type would not be inconsistent with the experimental facts, and would also lead to an R *vs* (F_2) curve which extrapolates to zero at zero F_2 concentration.

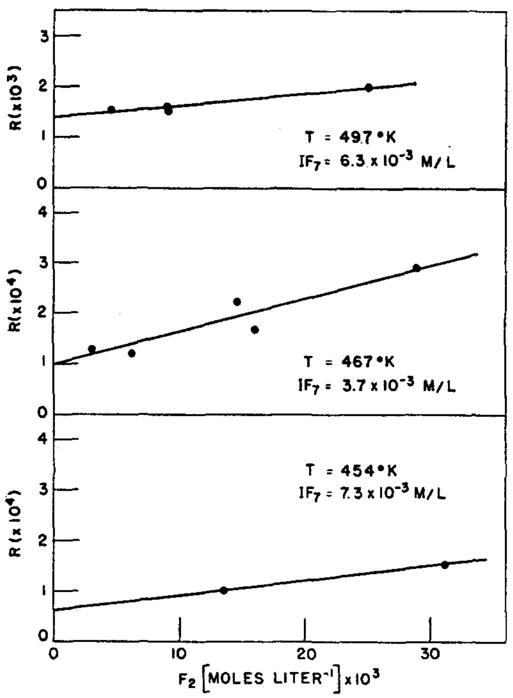

FIG. 5. IF_7-F_2 exchange. Rate *vs* F_2 concentration.

Since the homogeneous and heterogeneous components of the ClF_3-F_2 and IF_7-F_2 exchanges may thus be separated, it is possible to calculate the individual rate constants. The homogeneous rate constant k_1 is the slope of the straight line representing the homogeneous component of the exchange. For the heterogeneous path it is possible to calculate from the theoretical heterogeneous curve only the product of the rate constant times the adsorption coefficient of F_2, k_2x. Values are given in Table XI.

Apparent activation energies may be determined from the variation with temperature of experimental values of R at various concentrations of XF_n. It is also possible to obtain apparent activation energies for the separate homogeneous and heterogeneous components

TABLE XII. Apparent activation energies.

Exchange	E_a(hom) (kcal mole⁻¹)	E_a(het) (kcal mole⁻¹)	E_a(exp) (kcal mole⁻¹)	
			(XF_n)	
ClF_3-F_2	29	24	1×10^{-3}	22.1
			8	26.8
			15	29.0
IF_7-F_2	40	18.5	1×10^{-3}	20.5
			8	33.0
			15	36.4
BrF_5-F_2	...	23	1×10^{-3}	22.2
			5.5	22.4
			10	22.3

of the exchange from the temperature dependence of k_1, and from the temperature dependence of the product (k_2x). These are given in Table XII.

It might be expected that a homogeneous dissociative mechanism should have an activation energy comparable with the heat of dissociation of the halogen fluoride. The heats of dissociation of ClF_3, IF_7, and BrF_5 are 25, 28.5, and >42 kcal per mole.[3] Reference to Table XII shows that E_a(exp) for the ClF_3 and IF_7 exchanges are somewhat lower than ΔH^0 for these halogen fluorides at the lowest concentrations, and much lower than an estimated minimum ΔH^0 for all concentrations in the BrF_5 exchange. The existence of a heterogeneous path for exchange could account for this.

Attempts to find a change in rate due to a change in the nature and/or amount of surface were not entirely successful. A large number of experiments using different surfaces and additional surface area were run. The results were erratic; the largest effect noted was a factor of three in the rate. While the role of the surface in the exchange is not clear, there seems to be no doubt that it is involved in some way. Further work is in progress.

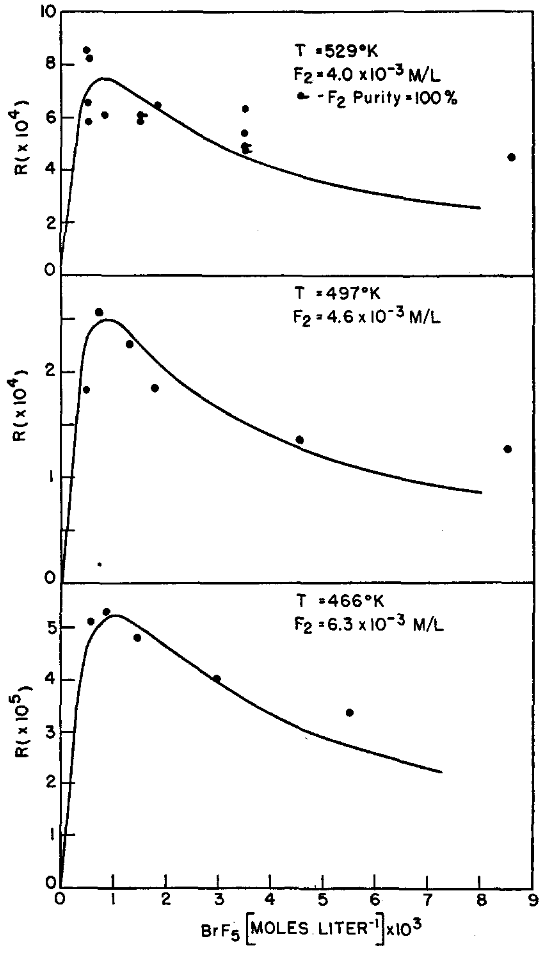

FIG. 6. BrF_5-F_2 exchange. Rate *vs* BrF_5 concentration. — = calculated heterogeneous exchange curve; ⊙ = experimental data.

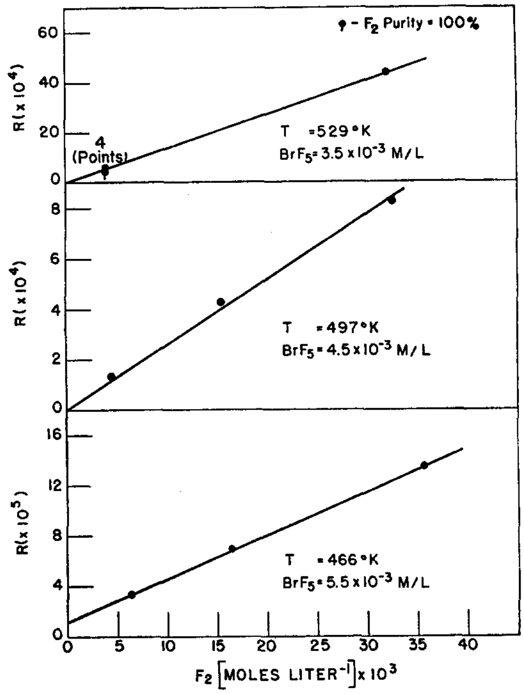

FIG. 7. BrF_5-F_2 exchange. Rate *vs* F_2 concentration.

Similar small surface effects have recently been observed in the deuterium-diborane exchange.[16]

The possibility that the air impurity in the fluorine might be responsible for the observed exchanges was eliminated by the use of fluorine of 100-percent purity in a number of the experiments. The rates thus observed are quite comparable to the rates obtained under similar conditions with the fluorine of 93.5-percent purity. Also, the possibility that some small amount of HF impurity in the fluorine might be responsible for the observed exchanges was eliminated by deliberately adding HF to an exchange mixture to the extent of 4 percent of the fluorine used. Figure 4 shows that the rate thus obtained falls on the smooth curve determined by the other experiments in this series.

A large number of alternative reaction mechanisms of the homogeneous type were considered with no success. For example, a simple homogeneous dissociative mechanism demands that the rate be independent of the fluorine concentration, which is contrary to the observed facts. It is possible, however, to develop a rate equation which qualitatively fits the experimental data by using the method of Spitalsky,[17] which assumes the reversible and simultaneous formation of two different activated complexes between F_2 and XF_n. This approach seems somewhat improbable because, while in the case of the ClF_3-F_2 exchange it might be possible to form a second activated complex between the dimer $(ClF_3)_2$ and F_2, it is difficult to believe that BrF_5 or IF_7 would be capable of forming such complexes.

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[16] P. C. Maybury and W. S. Koski, J. Chem. Phys. **21**, 742 (1953).

[17] E. Spitalsky, Z. physik. Chem. **122**, 257 (1926).

A simple atomic mechanism seems likewise improbable, since it would lead to a rate expression involving the square root of the fluorine concentration.[18]

It would thus appear that for the ClF_3-F_2 and IF_7-F_2 reactions the exchange occurs by a combined heterogeneous mechanism of the competitive type and a homogeneous mechanism involving the dissociation of the halogen fluoride. In the case of the BrF_5-F_2 exchange, a competitive heterogeneous mechanism would appear to explain the results.

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[18] The concentration of fluorine atoms resulting from thermal dissociation of F_2 may be estimated from the data given by R. N. Doescher [J. Chem. Phys. **20**, 330 (1952)] for the heat of dissociation of F_2. For a F_2 concentration of 12×10^{-3} mole/liter (about 10^{19} molecules/cc at 500°K) in the reaction vessel, there would be about 10^{14} F atoms/cc. This may be compared to the estimate given by Dodgen and Libby (reference 1) of 10^{12} F atoms/cc per 10^{19} F_2 molecules/cc present in the $HF-F_2$ exchange when it is carried out in the presence of ultraviolet light at room temperature, under which conditions no exchange was observed. Although the concentration of fluorine atoms in these exchanges appears to be large enough so that an atomic mechanism might exist, no success has been achieved in devising an atomic mechanism which would give a linear dependence of the rate on the fluorine concentration.

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Symmetry Classification of the Energy Levels of Some Triarylmethyl Free Radicals and Their Cations*

TING LI CHU AND S. I. WEISSMAN
Washington University, St. Louis, Missouri

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The absorption and luminescence spectra of triphenylmethyl, tri-p-xenylmethyl, phenyl-di-p-xenylmethyl, diphenyl-p-xenylmethyl, and their cations have been determined. Polarization of the luminescence of each substance under excitation by plane polarized light has been examined. Assignment of symmetry classifications to the energy levels of these substances has been attempted.

IN this paper we describe our studies of the spectra of a set of triarylmethyl free radicals and their positive ions. The experiments consist of observations of the absorption spectra, the fluorescence spectra, and polarizations of the fluorescence spectra under excitation by polarized light. From a combination of these observations and some assumptions which appear to be not excessively bizarre, we have attempted to assign symmetry classifications to the electronic levels of the molecules under study. These molecules are triphenylmethyl, diphenyl-p-xenylmethyl, phenyl-di-p-xenylmethyl, tri-p-xenylmethyl, and their positive ions.

EXPERIMENTAL PROCEDURES

The free radicals were prepared by standard procedures.[1,2] Pure tri-p-xenylcarbinol was provided by Professor Lipkin. Diphenyl-p-xenylcarbinol and phenyl-di-p-xenylcarbinol were prepared by appropriate Grignard reactions. Their melting points were 135°C and 150–151°C (uncorrected), respectively, as compared with the accepted values of 136°C and 151°C. Triphenyl methyl was prepared from commercial triphenyl-chloromethane which had been purified by vacuum sublimation.

The solvent for the free radicals was a mixture of toluene and triethylamine containing 20 percent by volume of triethylamine. The absorption spectra were measured both at room temperature and liquid nitrogen temperature with a Beckman model D. U. spectrophotometer.[3] The spectra at liquid nitrogen temperatures were checked by photography with an A.R.L. grating instrument. The fluorescence spectra were observed only from glassy rigid solutions at liquid nitrogen temperature. These were photographed with a Steinheil spectrograph.

The absorption and luminescence spectra of the free radicals are presented in Figs. 1–5, of the cations in Figs. 6–10.

Polarizations of the fluorescence were determined both by visual observation and by photography. The experimental arrangement, involving excitation in two almost contiguous strips by beams of equal intensity and mutually perpendicular polarization, has been described previously.[4]

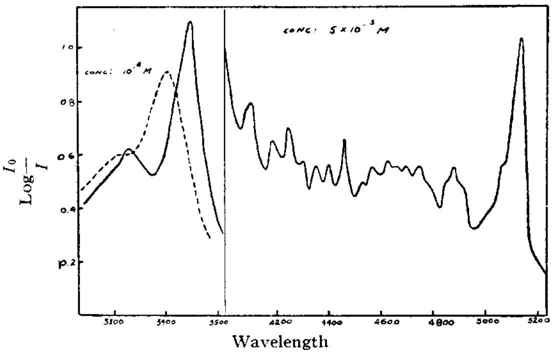

FIG. 1. Absorption spectrum of triphenylmethyl. Dashed curve at room temperature, solid curve at 77°K. One centimeter path length.

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* Assisted by the joint program of the U. S. Office of Naval Research and U. S. Atomic Energy Commission.

[1] Lewis, Lipkin, and Magel, J. Am. Chem. Soc. **66**, 1579 (1947).

[2] T. L. Chu and S. I. Weissman, J. Am. Chem. Soc. **73**, 4462 (1951).

[3] The free radicals were prepared under high vacuum. The absorption and fluorescence cells were in every case sealed off.

[4] S. I. Weissman, J. Chem. Phys. **18**, 1258 (1950).