The Photolysis of Cyanogen Chloride with a Mixture of Cyclohexane and Perdeuteriocyclohexane. A solution of cyanogen chloride (0.62 M), cyclohexane (0.97 M), and perdeuteriocyclohexane (0.83 M) in acetonitrile (1.9 ml) was degassed and irradiated for 4 hr. Glpc analysis (SE30, 110°) for (total) cyclohexyl cyanide gave a yield of 0.24 mmole (20.5%), and isolation of the unreacted hydrocarbon mixture (SE30, 70°) and analysis by the mass spectrum indicated that the cyclohexane contained 0.044 mg-atom of deuterium and that the perdeuterated material contained 0.051 mg-atom of hydrogen. The ratio of the number of exchanges to product formed was 0.84.

The reaction was repeated using a solution (1.6 ml) which was 0.72 M in cyanogen chloride and 0.35 and 0.30 M in cyclohexane and perdeuteriocyclohexane, respectively. An analogous analytical procedure showed that the yield of (total) cyclohexyl cyanide was 0.06 mmole (5.2%), of deuterium in the unreacted cyclohexane was 0.018 mg-atom, and of hydrogen in the perdeuteriocyclohexane was 0.008 mg-atom. The ratio of exchanges to formation of product was 0.86.

The Reaction of Cyanogen Chloride with *n*-Butane. To a solution of cyanogen chloride (0.30 M) and benzoyl peroxide (0.11 M) in acetonitrile (four 2.0-ml portions) was added *n*-butane (0.5 ml). The degassed solutions were heated to 98° for 3 hr. Glpc analysis for alkyl chlorides (UP, 70°), and for alkyl cyanides (UP, 125°) indicated the following yields: 1-chlorobutane, 0.3%; 2-chlorobutane, 6%; valeronitrile, 4%; α-methylbutyronitrile, 50%. The latter compound was isolated and identified by ir and nmr; the former three were identified by comparison of their retention times on glpc (UP and SE30) with those of authentic samples.

In a photochemical experiment a series of solutions of cyanogen chloride (3.3 M) in *n*-butane was degassed and irradiated for 2–6 hr. The products of the reaction were analyzed by glpc (UP, 115°). It was found that the ratio of valeronitrile to α-methylbutyronitrile varied according to the extent of the reaction. These results were summarized in Table I.

The Reaction of Cyanogen Chloride with Toluene. A solution of cyanogen chloride (8 mmoles) and benzoyl peroxide (0.27 mmole) in toluene (10 ml) was degassed and heated to 75° for 50 hr. Glpc analysis (neopentyl glycol succinate (NPGS), 190°) indicated the presence of benzyl cyanide (1.8%) and a sample was isolated by preparative glpc and identified by its ir.

Further experiments with a solution of cyanogen chloride (0.64 M) in toluene in the presence of varying quantities of benzoyl peroxide indicated that benzyl chloride was also formed. The optimum yield of benzyl cyanide was 10.8% (Bz_2O_2/CNCl = 0.72) and a "chain length" of 0.6 was found. The yield of benzyl chloride was always slightly less than that of benzyl cyanide. When the reaction of cyanogen chloride and toluene was photoinitiated, no benzyl cyanide could be detected.

The Photolysis of Chlorine with Benzyl Cyanide. A sample of benzyl cyanide was shown to be free of benzyl chloride and cyanogen chloride by glpc (SE30, NPGS). Chlorine was now bubbled into duplicate samples of the pure liquid (2.0 ml) in the dark until a saturated solution was obtained. The solutions were degassed and irradiated with light from an incandescent lamp in a Pyrex ampoule, until the color of chlorine had disappeared. The solution was now opened directly into the vacuum line and the products were fractionated[30] between three traps maintained at −63, −95, and −196°. Hydrogen chloride passed into the latter trap and was discarded. The contents of the −95° trap were analyzed for cyanogen chloride using the mass spectrometer, and an exact mass analysis showed the presence of cyanogen chloride in the peak at m^+/e 61 (calculated mass, 60.9720; found, 60.9719). Glpc analysis, using two columns (SE30, NPGS) of the residual liquid confirmed the presence of benzyl chloride in the mixture.

The Reaction of Cyanogen Chloride with Neopentane. A mixture of cyanogen chloride (10 mmoles), benzoyl peroxide (0.17 mmole), benzene (5 ml), and neopentane (4 ml) was degassed and heated to 75° for 51 hr. Glpc analysis (SF96, 85°) showed the presence of one product, of which a sample was collected by preparative glpc (SF96, 85°) and found to be β,β-dimethylbutyronitrile: nmr (CCl_4), τ 8.88 (singlet, 9 H), 7.85 (singlet, 2 H); ir (CCl_4), ν 2245 cm^{-1} (C≡N).

A series of reactions was carried out in acetonitrile (1.0 ml) containing cyanogen chloride (0.73 mmole), to which was added neopentane (0.5 ml) and varying quantities of benzoyl peroxide. The optimum yield of β,β-dimethylbutyronitrile was 45% (Bz_2O_2/ClCN = 0.9).

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The Exchange Reaction of Acetyl Fluoride and Acetyl Hexafluoroarsenate[1]

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Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada. *Received November 25, 1968*

Abstract: From the temperature dependence of the exchange rate of the methyl protons between acetyl fluoride and acetyl hexafluoroarsenate an Arrhenius activation energy of 11.0 ± 0.4 kcal/mol and a preexponential factor of $10^{8.9 \pm 0.3}$ were obtained. From the concentration dependence of the exchange rate the reaction was found to be one-half order in acetyl hexafluoroarsenate and zero order in acetyl fluoride.

There have been many proton magnetic resonance studies of carbonium ions which are stable in solution.[3] Information about the rates of exchange processes has been obtained from variable temperature studies.[4] However, few investigations have been made where the concentration of all exchanging species could be independently varied.[5] Such a procedure is advisable to determine the mechanism of the exchange reaction. Since the relatively unstable carbonium ions are usually prepared by dissolving the precursor in a very strongly acidic medium it has not been possible to control the relative concentrations of the exchanging species for these ions. In the present study it was

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(1) Presented in part at the 23rd Symposium on Structure and Molecular Spectroscopy at Columbus, Ohio, 1968.

(2) National Research Council Post Doctoral Fellow, 1967–1968.

(3) D. Bethell and V. Gold, "Carbonium Ions, an Introduction," Academic Press, New York, N. Y., 1967.

(4) D. M. Brouwer, C. MacLean, and E. L. Mackor, *Discussions Faraday Soc.*, 39, 121 (1965).

(5) H. H. Freedman, A. E. Young, and V. R. Sandel, *J. Am. Chem. Soc.*, **86**, 4722 (1964).

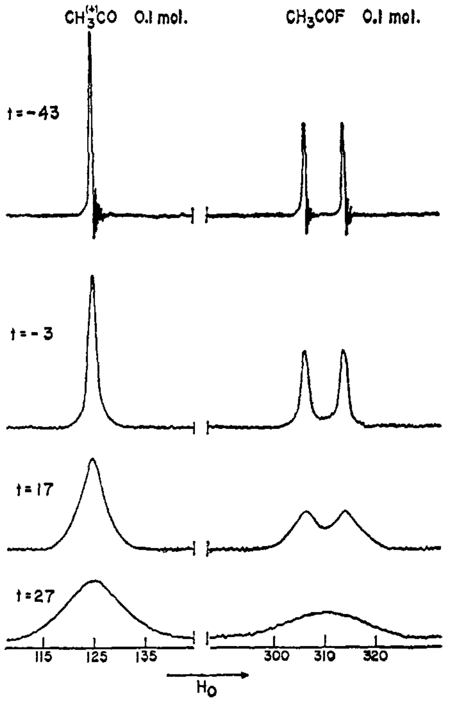

Figure 1. Temperature dependence of the proton resonance spectrum of a solution of acetyl fluoride and acetyl hexafluoroarsenate in sulfur dioxide. The peak positions are listed in hertz from methylene chloride.

found that the system acetyl hexafluoroarsenate plus acetyl fluoride was stable for a reasonable period of time, even at room temperature. Therefore it is possible to study the exchange reaction of this simple oxocarbonium ion in considerable detail. It has been shown by Olah and coworkers that in sulfur dioxide solution acetyl hexafluoroarsenate exists essentially completely as the ion pair.[6] Therefore with sulfur dioxide as solvent the exchange reaction is not complicated by transitions between donor–acceptor complex and ion pair.

Results and Discussion

The proton magnetic resonance spectrum of acetyl fluoride in sulfur dioxide solution is a symmetric doublet (J_{H-F} = 7.6 Hz, δ 2.30 ppm from tetramethylsilane), while that of acetyl hexafluoroarsenate is a singlet (δ 4.15 ppm). The spin-coupling constant and chemical shifts of these species are nearly independent of the temperature over the range of −40 to +27° used in the kinetic studies. The line widths were found to be equal to that of the reference, methylene chloride, and presumably attributable to the resolution of the spectrometer. The effect of temperature upon the spectrum of an equimolar solution of both species is shown in Figure 1. In order to obtain the lifetimes of the exchanging species from their spectra, theoretical spectra were calculated and compared with those obtained experimentally. The theoretical spectra were calculated with the same general matrix technique employed previously.[7] A comparison of experimental and theoretical spectra for the acetyl fluoride portion of the spectra of one sample is shown in Figure 2.

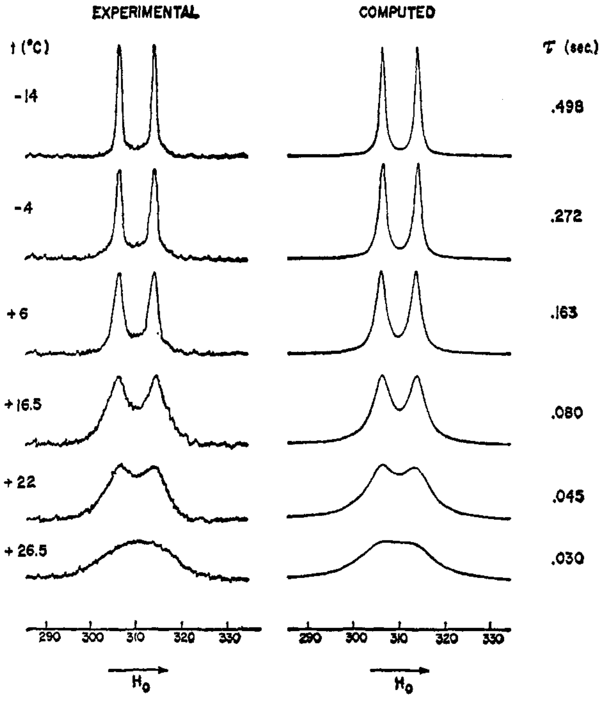

Figure 2. A comparison of experimental and theoretical spectra for the acetyl fluoride moiety.

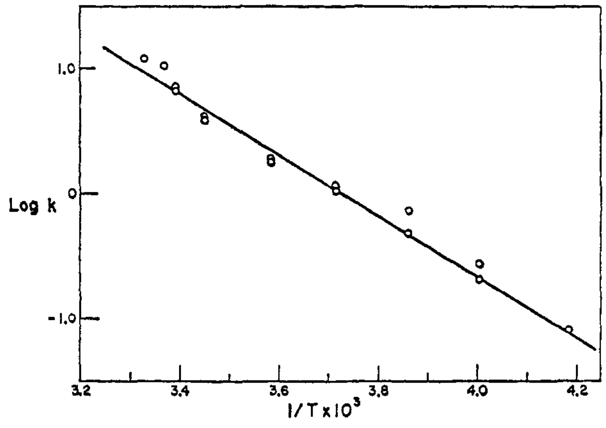

Figure 3. Temperature dependence of the rate of the exchange reaction.

In the slow exchange limit where the separation between the resonance peaks is considerably greater than the rate of conversion between two species it is possible to separately determine the lifetime of each species. The relationship of eq 1 between lifetimes and concentrations of the exchanging species must be obeyed. The symbols τ and C denote lifetime and

$$\tau_1/C_1 = \tau_2/C_2 \qquad (1)$$

concentration, respectively. Throughout the temperature range accessible in this study it was possible to determine separate lifetimes for each species. From the temperature dependence of the lifetime, averaged for both species, an Arrhenius activation energy of 11.0 ± 0.4 kcal/mol and a preexponential factor of $10^{8.9 \pm 0.3}$ were obtained. The experimental results for samples 0.1 *m* in each species are plotted in Figure 3.

The relationship between lifetime, as determined by magnetic resonance investigations, and rate of change

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[6] G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *J. Am. Chem. Soc.*, 84, 2733 (1962).

[7] S. Brownstein and J. Bornais, *Can. J. Chem.*, 46, 225 (1968).

Table I. Temperature and Concentration Dependence of CH_3COF and $CH_3CO^+AsF_6^-$ Lifetimes

$[CH_3CO^+AsF_6^-]$	$[CH_3COF]$	300°K		290°K		280°K	
		$\tau_{CH_3CO^+}$	τ_{CH_3COF}	$\tau_{CH_3CO^+}$	τ_{CH_3COF}	$\tau_{CH_3CO^+}$	τ_{CH_3COF}
0.105	0.211	0.030	0.057	0.077	0.150	0.15	0.32
0.106	0.107	0.026	0.030	0.071	0.080	0.17	0.16
0.107	0.052	0.028	0.014	0.077	0.038	0.20	0.11
0.054	0.108	0.019	0.047	0.052	0.133	0.12	0.30
0.027	0.106	0.0135	0.066	0.036	0.193	0.08	0.49

of concentration, measured in conventional kinetic studies, is given by eq 2. The exchange reaction of

$$d[X]/dt = [X]/\tau_X \qquad (2)$$

this investigation may be represented by

$$^*CH_3CO^+AsF_6^- + CH_3COF \rightleftharpoons {}^*CH_3COF + CH_3CO^+AsF_6^-$$

A perfectly general equation for the exchange reaction is

$$\frac{d[\overset{*}{C}H_3CO^+AsF_6^-]}{dt} = c[^*CH_3CO^+AsF_6^-]^x[CH_3COF]^y \qquad (3)$$

Substituting eq 2 into 3 yields

$$\tau_{CH_3COAsF_6} = \frac{1}{c}[CH_3CO^+AsF_6^-]^{1-x}[CH_3COF]^{-y} \qquad (4)$$

In an analogous manner the general equation for the concentration dependence of the lifetime of acetyl fluoride may be obtained. Experimentally it was found that the lifetime of acetyl hexafluoroarsenate depended upon its concentration to the one-half power and was independent of the concentration of acetyl fluoride. The half-order dependence on acetyl hexafluoroarsenate concentration is shown in Figure 4.

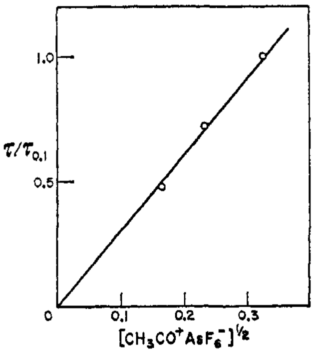

Figure 4. Concentration dependence of the rate of the exchange reaction.

In order to average the results for every sample at every temperature without a very complicated presentation the plot of Figure 4 was used. At any given temperature the ratio of rates for different samples should only depend upon the concentrations of exchanging species in these samples. Therefore this ratio may be averaged for all temperatures to obtain a more widely based, and hence more accurate, concentration dependence. Some of the data on which Figure 4 is based is presented in Table I.

The half-order dependence on acetyl hexafluoroarsenate concentration can be most easily explained by assuming that acetyl hexafluoroarsenate exists, in sulfur dioxide solution, primarily as an ion pair which is in rapid equilibrium with dissociated ions. It has frequently been shown that ionic compounds are usually present as ion pairs in solvents of low dielectric constant.[8] A half-order reaction involving anion exchange has also been explained by this postulate.[7] The equilibrium constant for dissociation of acetyl hexafluoroarsenate is given by

$$K = \frac{[CH_3CO^+][AsF_6^-]}{[CH_3CO^+AsF_6^-]} \qquad (5)$$

Therefore

$$[CH_3CO^+] = (K[CH_3CO^+AsF_6^-])^{1/2} \qquad (6)$$

Provided that the extent of dissociation is small the concentration of acetyl hexafluoroarsenate in solution will be essentially equal to that originally added to the sample. Substituting (6) into (4) where x is one-half and y is zero gives

$$\tau_{CH_3COAsF_6} = \frac{1}{cK^{1/2}}[CH_3CO^+] \qquad (7)$$

Therefore the temperature dependence of the rate of the exchange reaction does not give the activation energy for the rate-controlling step but rather a combination of this with the heat of formation of the ion pair from dissociated ions.

The observed rate law for the exchange reaction implies that the mechanism for the exchange is a rapid reversible dissociation of acetyl hexafluoroarsenate to yield separated ions. The acetyl ion then undergoes some type of rearrangement, perhaps a reorganization of the solvation shell, in the rate-controlling step of the reaction. This is followed by a rapid reaction of the appropriately structured acetyl ion with acetyl fluoride. There is other evidence from Raman spectroscopy for two types of acetyl ion in solution but the detailed structures are not known.[9] The proposed mechanism for the reaction can be represented by the following steps.

$$CH_3CO^+AsF_6^- \xrightleftharpoons{\text{fast}} CH_3CO_I^+ + AsF_6^- \qquad (A)$$

$$CH_3CO_I^+ \xrightarrow{\text{slow}} CH_3CO_{II}^+ \qquad (B)$$

$$CH_3CO_{II}^+ + \overset{*}{C}H_3COF \xrightarrow{\text{fast}} \overset{*}{C}H_3CO^+ + CH_3COF \qquad (C)$$

Since the postulated exchange mechanism has some novel features attempts were made to obtain further results which might confirm or disprove the above mechanism. One consequence of the preceding mechanism is that added hexafluoroarsenate ions should

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(8) W. F. Luder, P. B. Kraus, C. A. Kraus, and R. M. Fuoss, *J. Am. Chem. Soc.*, **58**, 255 (1936).

(9) A. Commeyras, private communication.

displace the dissociation equilibrium and lower the concentration of acetyl ions by the common ion effect. This should then cause a reduction in the exchange rate of acetyl hexafluoroarsenate. Unfortunately those hexafluoroarsenates which are soluble in sulfur dioxide exist almost entirely as the ion pair in solution. Therefore a negative result would not disprove the mechanism but a reduction in rate would be confirming evidence. It was found that addition of an equimolar quantity of tetra-*n*-butylammonium hexafluoroarsenate had no effect on the rate of exchange.

If the two different states of the acetyl ion involve a change in solvation the mechanism or rate of the reaction might change upon changing solvent. Acetyl hexafluoroarsenate is essentially insoluble in CH_2Cl_2 and SO_2F_2. A minor change in solvent was attempted by addition of another salt, tetra-*n*-butylammonium perchlorate. A rearrangement reaction occurred to yield acetyl perchlorate as neutral molecules. Its proton resonance peak is in the same position as those previously reported for acetyl complexes.[6] No exchange reaction was observed between acetyl perchlorate and acetyl fluoride at temperatures where the previous exchange reaction was rapid.

Experimental Section

Proton resonance spectra were obtained at 100 MHz on a Varian Associates HR100 spectrometer. Probe temperatures were calibrated with a copper–constantan thermocouple in a dummy sample tube. Methylene chloride, purified and stored over Linde Molecular Sieve 4A in a container on the vacuum line, was used as internal reference. Tetramethylsilane is unsuitable since it slowly reacts with arsenic pentafluoride to yield trimethylsilyl fluoride. Arsenic pentafluoride (Ozark-Mahoning) and anhydrous sulfur dioxide (Matheson) were stored over P_2O_5 in bulbs on the vacuum line. Acetyl fluoride was prepared according to the literature[10] and kept frozen when not being used. It was necessary to carefully bake the vacuum system prior to sample preparation in order to get adequately pure samples. If this precaution is not followed eq 1 is not obeyed, presumably because of other exchange pathways for the acetyl ion. Throughout this investigation only samples which obeyed eq 1 were used. The occasional sample which deviated was discarded and another prepared. The extent of agreement with eq 1 is shown in part by Table I. The data were fitted by least-square techniques and the listed errors are standard deviations.

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The Reaction of Organomercuric Halides with Dicobalt Octacarbonyl. A New Ketone Synthesis[1]

Dietmar Seyferth and Ralph J. Spohn[2]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received January 9, 1969*

Abstract: Many organomercuric halides react with dicobalt octacarbonyl in tetrahydrofuran solution at room temperature to give the ketone ($R_2C{=}O$) derived from R in RHgX, $Hg[Co(CO)_4]_2$, Co(II) halide, and carbon monoxide. The reaction proceeds rapidly and is of good preparative utility. The scope and limitations of this new ketone synthesis have been defined and the probable mechanism involves the following steps: solvent-induced redox disproportionation of dicobalt octacarbonyl to give $THF \cdot Co(CO)_4^+$ and $Co(CO)_4^-$; nucleophilic displacement of halide ion from mercury by the latter; electrophilic cleavage of the C–Hg bond in the $RHgCo(CO)_4$ formed (or in its disproportionation product, R_2Hg) by $THF \cdot Co(CO)_4^+$, forming $RCo(CO)_4$; organic group migration in the latter, producing $RCOCo(CO)_3$; and reaction of the latter with $RCo(CO)_4$ to give the ketone and cobalt carbonyl. Diphenylmercury also reacts with dicobalt octacarbonyl in THF to give benzophenone and $Hg[Co(CO)_4]_2$.

During a study of the possible extension of our recently observed dihalocarbene insertion into the Sn–Sn bond of hexamethylditin[3] to other metal–metal bond systems, the reaction of phenyl(trichloromethyl)mercury with dicobalt octacarbonyl was investigated.[4] The products obtained were $Hg[Co(CO)_4]_2$, chloromethinyltricobalt enneacarbonyl, cobalt(II) chloride, chloroform, and benzophenone. The presence of chloroform in the reaction mixture spoke for a CCl_3^- displacement from mercury at some stage during this reaction, nucleophilic displacement of CX_3^- from mercury being known to be a very facile process.[5,6] Further reaction of chloroform with dicobalt octacarbonyl no doubt was responsible for the small amount of chloromethinyltricobalt enneacarbonyl produced.[7] The formation of benzophenone suggested to us that organocobalt intermediates were involved and raised the question if the process exemplified by this reaction might not be of synthetic utility. Accordingly, a more detailed investigation was undertaken. Since the trichloromethyl group did not seem to be essential to the process to be studied and since nucleophilic displacement of halide ion from mercury occurs very readily under mild conditions,[8] it was decided to devote our further attention to a study of the action of dicobalt octacarbonyl on organomercuric halides.

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(2) National Institutes of Health Predoctoral Fellow, 1966 to present.

(3) (a) D. Seyferth and F. M. Armbrecht, Jr., *J. Am. Chem. Soc.*, **89**, 2790 (1967); (b) D. Seyferth, F. M. Armbrecht, Jr., and B. Schneider, *ibid.*, **91**, 1954 (1969).

(4) D. Seyferth, J. Y.-P. Mui, and R. J. Spohn, unpublished work.

(5) D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, *J. Am. Chem. Soc.*, **89**, 959 (1967).

(6) D. Seyferth, M. E. Gordon, and R. Damrauer, *J. Org. Chem.*, **32**, 469 (1967).

(7) (a) W. T. Dent, L. A. Duncanson, R. G. Guy, W. H. B. Reed, and B. L. Shaw, *Proc. Chem. Soc.*, 169 (1961); (b) G. Bor, L. Markó, and B. Markó, *Chem. Ber.*, **95**, 333 (1962).

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