The reaction of trimethylarsine–trimethylsilylmethylene[4] with trimethylsilanol leads to a desilylation of the ylid with formation of hexamethyldisiloxane

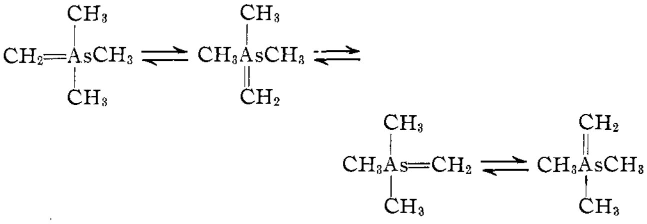
$$(CH_3)_3SiCH{=}As(CH_3)_3 + (CH_3)_3SiOH \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + \underset{\text{I}}{(CH_3)_3As{=}CH_2}$$

The high tendency of formation of the siloxane linkage promotes the reaction to proceed according to this equation. After evaporation of the siloxane under vacuum I is easily purified by sublimation at 30–35° under 0.1 mm of pressure. The compound forms beautiful colorless crystals, mp 33–35°, which are sensitive to air and moisture. On exposure to the atmosphere, a brown-violet color is developed almost instantaneously. Slow decomposition is also observed on heating above 38°. From cryoscopic molecular weight determinations I appeared to be monomeric in benzene solution.

As in the case of the phosphorus analog,[1] the proton nmr spectra of I merit special interest. The spectrum of a benzene solution at room temperature shows the expected two lines at $\delta_{CH_3} = -49$ and $\delta_{CH_2} = +11.5$ cps[5] with relative areas 9:2. The CH_2 resonance appears at very high field, thus indicating a preference of the ylid form (B) for the description of bonding according to the formulas

$$\underset{\text{A}}{(CH_3)_3As{=}CH_2} \longleftrightarrow \underset{\text{B}}{(CH_3)_3\overset{\oplus}{As}{-}\overset{-}{C}H_2^{\ominus}}$$

The CH_2 as well as the CH_3 signal clearly shows a line broadening at elevated temperatures, which is reversible on cooling. This phenomenon again[1] has to be interpreted by the assumption of a rapid proton exchange between both structural sites above room temperature



$$CH_2{=}\overset{CH_3}{\underset{CH_3}{As}}CH_3 \rightleftharpoons CH_3\overset{CH_3}{\underset{\underset{CH_2}{\|}}{As}}CH_3 \rightleftharpoons CH_3\overset{CH_3}{\underset{CH_3}{As}}{=}CH_2 \rightleftharpoons CH_3\overset{\overset{CH_2}{\|}}{\underset{CH_3}{As}}CH_3$$

The rapid decomposition of I above 60° prevents observation of the collapse and coalescence of both peaks, which formerly in $(CH_3)_3PCH_2$ has been observed without difficulties,[1] owing to the greater thermal stability of the latter. Merging of the resonances can be accomplished, however, already at room temperature on addition of traces of a protic species, *e.g.*, methanol. Obviously, proton catalysis favors rapid intermolecular proton exchange between the ylid molecules, for which now a single sharp line is observed. As expected, this resonance no longer shows $^1H-^{13}C$ satellites.

Chemically, I resembles its phosphorus analog.[1] It is alkylated by methyl iodide, almost quantitative yields of trimethylethylarsonium iodide being formed

$$(CH_3)_3As{=}CH_2 + CH_3I \longrightarrow [(CH_3)_3AsC_2H_5]^+I^-$$

The reaction with hydrogen halides converts I into tetramethylarsonium halides.

On prolonged standing at room temperature a 1:1 mixture of I and trimethylphosphine shows an interesting "transylidation" reaction, resulting in an equimolar mixture of trimethylarsine and (trimethylphosphine)-methylene

$$(CH_3)_3As{=}CH_2 + (CH_3)_3P \longrightarrow (CH_3)_3As + (CH_3)_3P{=}CH_2$$

This reaction is easily followed by nmr spectroscopy.

Among a number of products, which are formed under the thermal decomposition of I, trimethylarsine and ethylene have been detected by vapor phase chromatography to be the main components.

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[4] N. E. Miller, *Inorg. Chem.*, **4**, 1458 (1965).

[5] At 60 Mc, relative to TMS externally, positive sign for higher field.

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A Novel Synthesis of Bis(fluorocarbonyl) Peroxide[1]

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Bis(fluorocarbonyl) peroxide was first reported by Schumacher and co-workers.[2] Their elegant synthesis uniting fluorine, carbon monoxide, and oxygen at room temperature to give nearly quantitative yields of bis(fluorocarbonyl) peroxide has yet to be matched for convenience and simplicity. However, their preparation still requires handling elementary fluorine in the same system with carbon monoxide, introducing some potential hazard.

In the course of investigations of the chemistry of oxalyl fluoride, it was discovered that photolysis of oxalyl fluoride in the presence of oxygen led to the formation of bis(fluorocarbonyl) peroxide in yields approaching 50%. This discovery is consistent with Schumacher's proposed mechanism for the formation of the peroxide,[3] involving fluorocarbonyl groups which combine with oxygen.

Experimental Section

Oxalyl fluoride was prepared by treating oxalyl chloride with sodium fluoride in acetonitrile at reflux, essentially employing the method of Tullock and Coffman.[4] The crude product collected at −183° was found to be contaminated with carbonyl fluoride, carbon dioxide, and acetonitrile. The material was warmed to −78°, and materials volatile at that temperature were allowed to expand into a conventional vacuum system of 350-cc volume. The sample tube was closed and the volatiles pumped away. This procedure was repeated until the residual vapor pressure at −78° fell substantially below 1 mm. The sample was then

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[1] Presented, in part, at the Northwest Regional Meeting of the American Chemical Society, Richland, Wash., June 1967.

[2] A. Arvia, P. Aymonino, C. Waldow, and H. J. Schumacher, *Angew. Chem.*, **72**, 169 (1960).

[3] J. Heras, A. Arvia, P. Aymonino, and H. Schumacher, *Z. Physik. Chem.* (Frankfurt), **28**, 250 (1961).

[4] G. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).

allowed to warm and distil slowly from one trap to another through the vacuum line. Approximately the first 1% and last 5% were set aside.

This procedure was repeated on the middle fraction several times until the product was found to be free from impurities on the basis of its infrared spectrum[5] and fractional codistillation[6] of a sample.

Irradiations were carried out in a 2-l. Pyrex glass flask equipped with a quartz finger containing a water-cooled Hanau 350-w mercury-arc lamp.

In a typical run 13.2 mmoles of oxalyl fluoride was condensed into the irradiation flask, 59.3 mmoles of oxygen was added, the flask was allowed to warm to room temperature, and irradiation was begun. After about 12 hr, irradiation was terminated. The products were bled through a trap held at −183° and substances volatile at that temperature were pumped away. The remaining materials were separated by fractional codistillation and identified by infrared spectroscopy. The amounts were: 5.0 mmoles of COF_2 and SiF_4 (combined), 9.9 mmoles of CO_2, 0.4 mmole of $C_2O_4F_2$ impure with $C_2O_2F_2$, and 6.1 mmoles of pure $C_2O_4F_2$ (46% yield).

Bis(fluorocarbonyl) peroxide was identified by comparison of its infrared spectrum[7] with that of a sample prepared using Schumacher's synthesis, by its vapor density molecular weight (theoretical 126, found 129), and by liberation of iodine from aqueous potassium iodide.

It is probable that higher yields of the peroxide could be obtained by irradiating for shorter times and recycling the unreacted oxalyl fluoride after separation from $C_2O_4F_2$. Quantitative conversion is unlikely, however, since both oxalyl fluoride and bis(fluorocarbonyl) proxide decompose irreversibly under prolonged ultraviolet irradiation.

$$(FCO)_2 \xrightarrow{h\nu} COF_2 + CO$$

$$(FCO_2)_2 \xrightarrow{h\nu} COF_2 + CO_2 + {}^1/_2O_2$$

Bis(fluorocarbonyl) peroxide has been reported to decompose, and even explode at elevated temperatures.[1] Though no difficulties were encountered during this work, the compound was treated as if hazardous, and care was taken to maintain sample temperatures below 30°, with adequate shielding during manipulations.

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(5) D. E. Milligan, M. E. Jacox, A. M. Bass, J. J. Comeford, and D. E. Mann, *J. Chem. Phys.*, **42**, 3187 (1965).

(6) G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

(7) A. T. Arvia and P. J. Aymonino, *Spectrochim. Acta*, **18**, 1299 (1962).

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Rate–pH Profile for the Dissociation of Iron(II)- and Cobalt(II)-2,2′,2″-Terpyridine Complexes

By R. Farina, R. Hogg, and R. G. Wilkins[1]

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The dependence on pH of the rates of acid dissociation (hydrolysis) of metal complexes with a variety of bidentate ligands has been well studied.[2,3] It is believed that the proton acts as a scavenger for one released end of the bidentate ligand, giving a moderate accelerating effect on the rate with decreasing pH. Eventually a limiting rate is reached in sufficiently high acid concentration and the first-order rate constant in these conditions is equated to that of the metal–ligand bond rupture. The mechanism for acid dissociation of bidentate ligands capable of protonation should be equally adaptable to multidentate ligands also.[2] We report here on the effect of acid concentration on the dissociation of metal complexes containing the terdentate ligand 2,2′,2″-terpyridine, using mainly $M(terpy)_2^{2+}$ ions and M = Fe and Co

$$M(terpy)_2^{2+} \rightleftharpoons M(terpy)(H_2O)_3^{2+} + terpy \qquad (1)$$

Experimental Section

Kinetics.—The rate of dissociation of $Fe(terpy)_2^{2+}$ in $[H^+] <$ 0.2 *M* and of $Co(terpy)_2^{2+}$ in neutral (pH ~6) solutions was measured by ^3H–terpy exchange experiments.[4] The dissociation of $Co(terpy)_2^{2+}$ in dilute acid was effected by addition of ferrous ions.[5] Complete dissociation of $Fe(terpy)_2^{2+}$, $Co(terpy)_2^{2+}$, $Co(bipy)_3^{2+}$, and $Co(terpy)^{2+}$ in suitable concentration occurs at $[H^+] > 0.1$ *M* and was easily followed with a Cary 14 or a glass Lucite stopped-flow apparatus spectrally at 550, 520, 425, and 420 mμ, respectively. Dissociation of $Fe(terpy)_2^{2+}$ in high base concentration was also followed at 550 mμ in the presence of EDTA (~10^{-4} *M*) to maintain a homogeneous solution,[6] although apparently this is not essential.[7] Complexes used in this study were prepared as described previously.[4] Excellent first-order kinetic plots were obtained in all cases. In all runs $[H^+]$ remained constant.

Results and Discussion

We can be certain that we are measuring reaction 1 in the acid dissociation experiments since the mono species both is less absorbing and dissociates at a slower rate than the bis. In the isotopic exchange experiments, also, only the equilibrium in (1) contributes to ligand interchange.[8] The first-order dissociation rate constants (k_{obsd}) for a number of complexes and conditions are shown in Table I. The variation of k_{obsd} with pH for the $Fe(terpy)_2^{2+}$ and $Co(terpy)_2^{2+}$ ions can be accommodated by the mechanism[9] shown in Scheme I. Stationary-state conditions are assumed, with B, C, D, and E in very small concentration.[10]

In the low $[H^+]$ region where dissociation follows the route A → B → C → products, the value of k_{obsd} is pH independent, and it is easily shown that

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[1] Author to whom inquiries should be addressed at the State University of New York at Buffalo.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 216.

(3) A. G. Sykes, "Kinetics of Inorganic Reactions," Pergamon Press Ltd., London, 1966, p 236.

(4) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962).

(5) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).

(6) D. W. Margerum, *J. Am. Chem. Soc.*, **79**, 2728 (1957).

(7) J. Burgess and R. H. Prince, *J. Chem. Soc.*, 6061 (1965).

(8) R. G. Wilkins and M. J. G. Williams, *J. Inorg. Nucl. Chem.*, **6**, 52 (1958).

(9) k_3, k_4, and k_5, as well as k_8, k_9, and k_{10}, may be composite first-order rate constants involving both terminal and middle nitrogen–metal bond rupture and formation. It is understood that another terpyridine molecule is coordinated to M throughout the reaction.

(10) As judged from pH measurements, there is no rapid production of protonated species when $Fe(terpy)_2^{2+}$ (0.01 *M*) is acidified (pH 2).