cation it is necessary to heat the solutions for a short time. Conductivity measurements on a dimethyl sulfoxide solution of $[(C_6H_5)_2I]_2PtCl_4$ indicate very little change in electrolyte concentration in 3 weeks at room temperature; the conductivity drops rapidly at 150°, however. A color change (from orange to yellow) within the first hour at room temperature indicates that significant coordination of solvent occurs in this time. We conclude, then, that chloride ion and not chlorobenzene leaves the coordination sphere.

From dimethyl sulfoxide solutions we isolate $[Pt(DMSO)_2Cl_2]$. The infrared spectrum of this complex indicates it to be identical with the compound reported by Cotton, *et al.*[3]

The reaction in hot pyridine leads to the formation of the expected product, $[Pt(py)_4]Cl_2$, with no apparent contamination by $(C_6H_5)_2I^+$ salts. Heating $[(C_6H_5)_2I]_2PtCl_4$ in dimethylformamide gives an oil apparently containing coordinated solvent. The organic solubility of this substance makes it a promising intermediate for synthetic work.

Further work on these interesting salts is currently in progress in our laboratories.

Acknowledgment.—The author is indebted to Dr. Samuel J. Huang of this department for first bringing to his attention the reactivity of the diaryliodonium salts.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA

Photochemical Fluorinations of C_2N_2 and $R_fN{=}SF_2$ with N_2F_4[1]

BY R. D. DRESDNER, JACK MERRITT, AND JOYCE P. ROYAL[2]

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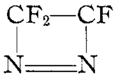
The properties of N_2F_4 and both isomers of N_2F_2 have been more than adequately described recently.[3] The main features of their properties that are applicable to this work are the facts that N_2F_4 is in equilibrium with the free radical NF_2 and that the K_p for the process at 25° is very small and that both N_2F_4 and *cis*-N_2F_2[4] absorb readily in the range between 2150 and 2250 Å. while NF_2 absorbs mainly at about 2600 ± 50 Å. A number of recent papers on the fluorination–difluoramination reaction in which the NF_2 radical is postulated as the main excited species have reportedly made use of low-pressure lamps which emit largely in the 2537 Å. range and not at all in the lower ranges, a factor that would favor activation of the free radical, NF_2.[5-7] The authors in the last paper also succeeded in preparing NF_2SF_5 in 30–35% yields from N_2F_4 and SF_4 and N_2F_4 and SF_5Cl as well as the most interesting $CF_3SF_4NF_2$ from CF_3SF_3 and N_2F_4. The difluoroaminosulfur pentafluoride was prepared previously *via* thermal free radical reactions using N_2F_4 and S_2F_{10}.[8,9]

Several fluorinations of cyanogen with different fluorinating agents are reported in the current chemical literature. Bigelow[10] has indicated that even under the most favorable conditions N–C–C–N chain retention, as $(NF_2CF_2)_2$, does not exceed 22% in the direct fluorination of cyanogen. Using AgF_2 as the fluorinating agent Emeléus and Hurst[11] found that, under optimum conditions, a 90% yield of the cyclic diazo compound, , was obtained, while CoF_3 as the fluorinating agent tended to give the same products in kind and distribution as were obtained with free fluorine. There seems little doubt as to the ultimate free radical nature of the mechanisms for the reactions with these three fluorinating agents.

In the course of the work reported in this paper the ultraviolet spectra of all the substances used were obtained. It is of interest to note that each showed strong absorptions in the range of 2100–2300 Å., a region not incompatible with the source used in this work.

Initial studies involving the photoexposure of $R_fN{=}SF_2$ indicated little or no reaction was occurring without ultraviolet light over periods of time equal in extent to the reaction periods with N_2F_4 using ultraviolet light. In Table I are found data on the reaction conditions and final results of the photoreactions between the iminosulfur difluorides and N_2F_4 using a high-pres-

TABLE I

CONDITIONS AND RESULTS OF THE PHOTOREACTIONS INVOLVING $R_fN{=}SF_2$ AND N_2F_4

Reagent	Mole ratio N_2F_4/ reagent	Moles of N_2F_4	Total initial press., mm.	Irradiation time, hr.	—Product yields,[a] %—		
					NF_2SN_5	R_fF	N_2
$CF_3N{=}SF_2$	1.5	0.054	140	16.5	93	100	99
$C_2F_5N{=}SF_2$	1.5	0.048	130	31.0	65	100	98
$C_3F_7N{=}SF_2$	1.3	0.048	130	23.3	66	100	98

[a] Other identifiable products were SOF_2, SiF_4, SF_6, and *cis*-N_2F_2. Only SOF_2 was present in the final gas reaction products in excess of 3 mole % of the mixture. Main stoichiometry: $R_fN{=}SF_2 + {}^3/_2N_2F_4 \rightarrow R_fF + NF_2SF_5 + {}^3/_2N_2$.

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[2] Part of the material in this paper has been abstracted from the M.S. thesis of Miss Royal, graduate student in chemistry at the University of Florida.

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sure mercury source with the transformer primary voltage maintained at 125 v.

When pure cyanogen was irradiated at about 150 mm. pressure with the high-pressure mercury source, about 11% was converted to paracyanogen in 15 hr. The polymer condensed more or less uniformly throughout the system. No significantly observable quantities of paracyanogen were observed in any of the reactions in which a mixture of cyanogen and N_2F_4 were studied. Mixtures of cyanogen and N_2F_4 did not react detectably over a period of 15 hr. without ultraviolet light exposure. Table II lists the conditions and results of a set of typical photoreactions between cyanogen and N_2F_4. It will be noted that retention of the N–C–C–N chain varies with the N_2F_4 concentration such that the percentage chain retention increases from 71 to 93% as the N_2F_4 concentration initially decreases from 67 to 34 mole %. The consecutiveness of the reactions can be demonstrated by the following data: In the reaction in which almost equimolar amounts of reactants were used the amount of nitrile produced increased as a function of time until it reached a maximum at 4.3 hr. of 14 mmoles and dropped to 12 mmoles in 7.5 hr.; meanwhile the concentration of the perfluorodiamine rose gradually as a function of time such that in 4.3 hr. it was 8 mmoles and 12 mmoles in 7.5 hr. The concentrations of the other materials present at the indicated times are consistent with a material balance correct to about 5%. Again, using the time of 4.3 hr. as a criterion, 3 mmoles of perfluoroethylamine was present while the amount of dinitrogen tetrafluoride had fallen to 8.5 mmoles, consistent with the formation of 36 mmoles of nitrogen. To complete the material balance, at this time there was present 23 mmoles of cyanogen.

TABLE II

CONDITIONS AND RESULTS OF PHOTOREACTIONS INVOLVING C_2N_2 AND N_2F_4

mmoles of reactants		Reaction press., mm.		Reaction time,	mmoles of products[a]						
C_2N_2	N_2F_4	Initial	Final	hr.	C_2N_2	N_2F_4	N_2	A	B	C	D
44	89	210	213	12.9	0	10	76	2	29	12	2
46	45	141	137	7.5	18	2	43	12	12	3	1
44	23	105	102	12.5	34	5	17	10	3	1	...

[a] A = NF_2CF_2CN, B = $(NF_2CF_2)_2$, C = $C_2F_5NF_2$, and D = CF_4, NF_3, and *cis*-N_2F_2.

The presence of SOF_2 as a product of the photoreactions with the fluorocarbon iminosulfur difluorides appears to be a result of either the reaction of N_2F_4 or NF_2SF_5 with the glass vessel. As the vessel did tend to show increased etching with time of use (despite cleaning between uses) the lesser amount of SOF_2 detected in the $CF_3N{=}SF_2$ reaction may be due to either the shorter reaction time or the greater imperviousness of the vessel as this reaction was the last of four experiments in a series with the same vessel.

The compound NF_2CF_2CN, N,N-difluoroaminoperfluoroacetonitrile, is a gas at room conditions and seems to be thermally stable in glass at 25°. Although perfluoroethylenediamine has never been reported to be unstable, a very pure sample stored in liquid nitrogen over a several-week period of time exploded quite violently when the dewar in which it was stored was agitated only slightly. It is not certain what catalyzed this behavior. Simple thermochemical calculations indicate that it would be most unstable to CF_4 and N_2. It is of interest to note that the CF_3 positive ion is most prominent in the mass spectral patterns of both NF_2CF_2CN and $NF_2CF_2CF_2NF_2$. This behavior is not manifested in the so-called hydrogen analogs. The implication seems to be that, in the time that is required to leave the ion chamber of the mass spectrometer, some activated species undergo at least C–C bond cleavage, C–F or N–F bond cleavage, and fluorine migration to form a CF_3^+ ion. The apparent stability of this ion may be related to its strong similarity to BF_3 and the fact that some double-bond character exists in the C–F bonds.

Experimental

All reactions were run in a 12-l., round-bottomed, Pyrex flask with a single ground-glass neck joint, through which was inserted an all-quartz cold finger, which was cooled with a flow of water. The cold finger was of such dimensions that the Hanovia Model 54A36 (S654A) ultraviolet lamp was completely within the flask when it was in operation. The lamp was operated by a Hanovia Model 7654-I transformer with the primary voltage maintained at 115–125 v. with a Variac. The lamp input was rated at 200 w. with an output of 25 w. of visible and ultraviolet radiant energy. The various ultraviolet emission lines in Å. and their intensities in watts are: 3660 (3.1), 3341 (0.36), 3130 (2.3), 3025 (0.86), 2967 (0.48), 2894 (0.20), 2804 (0.30), 2753 (0.14), 2700 (0.14), 2652 (0.64), 2571 (0.20), 2537 (1.10), 2482 (0.20), 2400 (0.20), 2380 (0.12), 2360 (0.08), 2320 (0.03), and 2224 (0.03).

The flask was loaded from and unloaded to a standard vacuum line. During the reaction the flask was adapted to another small vacuum line which lead to an analytical v.p.c. unit. The system was arranged so that about 7-ml. aliquots of the reaction mixture could be analyzed at frequent intervals. The aliquots were taken at the pressure of the reaction and swept into the v.p.c. unit with He carrier gas. Three different columns were used in this work: column A was an 8-ft., 0.25-in. o.d., copper tube filled with 25 wt. % dinonyl phthalate (DNP) on Chromosorb; column B was an 8-ft., 0.25-in. o.d., copper tube containing 25 wt. % silicone oil 220 on Chromosorb; and column C was a 40-ft., 0.25-in. o.d., copper tube packed with a mixture of 25 wt. % silicone oil 220 and 25 wt. % DNP each on Chromosorb in the weight ratio of 63:37, respectively. This ratio was determined by the mixed bed method.[12]

All infrared spectra were obtained on a Perkin-Elmer Model 137B Infracord.

Mass spectral data were obtained on a Bendix Model 14 time-of-flight mass spectrometer.

All n.m.r. spectra were obtained on a Varian A-60 instrument operating with a frequency of 56.4 Mc. and using trifluoroacetic acid as the external standard.

Cyanogen gas was purchased from the American Cyanamid Co., and we are grateful for the special effort made to provide this chemical.

Dinitrogen tetrafluoride was purchased from Air Products and Chemicals Corp. The main impurities were a very small amount

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of C_2F_6 and an indefinite amount of nitrogen which had to be removed before use.

The fluorocarbon iminosulfur difluorides were prepared from SF_4 and NaSCN or the appropriate fluorocarbon nitriles.[13] Prepurification of SF_4, purchased as technical grade, lead to the need for less drastic conditions in their preparation.

In general the irradiation system was loaded to a given pressure and the amount of material was determined from a knowledge of the volume of the system. The composition of mixtures was determined on the assumption that no associative interactions were occurring at well below an atmosphere of pressure. These are reported in Tables I and II. In almost every instance what appeared to be short—up to 1 hr.—induction times were observed. Whether this was inherent in the photoreaction or a function of the sampling system was never completely ascertained. The residual gas in the reaction system, at the end of certain reactions, was purged of noncondensables and the condensables were separated by semipreparative vapor phase chromatography in order to obtain adequate amounts of pure samples of the various materials for an unambiguous identification.

NF_2SF_5 was identified by its molecular weight and n.m.r. and infrared spectra, which were identical with those previously reported.[8]

$NF_2CF_2CF_2NF_2$ was identified from its molecular weight (203) and its mass spectrum, which was most similar to that previously reported.[10] The structure was confirmed by its n.m.r. spectrum [CF_2 (39.9 p.p.m. triplet) and NF_2 (-92.4 p.p.m. broad band) with peaks of equal area] and its infrared spectrum which (in cm.$^{-1}$) is: 1295 (m), 1235 (vs), 1190 (ms), 1165 (s), 1140 (ms), 1065 (w), 975 (ms), 950 (s), 925 (vs), 865 (s), 765 (s).

NF_2CF_2CN was identified from its molecular weight (130), n.m.r. spectrum [CF_2 (14.9 p.p.m. triplet) and NF_2 (-103 p.p.m. broad band) with peaks of equal area], and its infrared spectrum, which is (in cm.$^{-1}$): 2240 (s), 1220 (vvs), 1130 (s), 990 (vs), 933 (vs), and a weak band at 705–695. *Anal.* Calcd.: C, 18.5; F, 58.4. Found: C, 18.3; F, 58.9. The following vapor pressure data were determined for this compound [T (°K.), p (mm.)]: (193°, 38), (200°, 65), (207°, 110), (214°, 182), (227°, 359), (229°, 392), (237°, 613), (238°, 690). Extrapolation of the log p_m *vs.* $1/T$ plot results in a normal boiling point of 241°K. or -32°C. The straight line relationship fits the equation $\log p_{mm} = -1250/T + 8.05$. This relationship gives a heat of vaporization of 5740 cal./mole and a Trouton's constant of 23.4, implying some minor nonideal behavior. The mass spectrum which was obtained after the material was identified had the following characteristics (mass, ion, relative intensity): (76, CF_2CN, 100), (69, CF_3, 30), (23, CF, 23), (50, CF_2, 10), (90, CF_2N_2, 10), (83, CF_2N, 7), (45, CNF, 6), (33, NF, 5), (43, C_2F, 4), (52, NF_2, 4), (57, CFCN, 4).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA

π-Complexes of Cyclopentadienylmanganese Tricarbonyl with Acrylonitrile and Butadiene

BY M. L. ZIEGLER AND R. K. SHELINE[1]

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When solutions of cyclopentadienylmanganese tricarbonyl and a ligand in pentane, hexane, or cyclohexane are exposed to ultraviolet radiation, both π[2] and σ[3,4] complexes can be synthesized depending on the nature of the ligand utilized.

If a ligand is used which contains two or more π-bonding groups or both σ-[5-8] and π-bonding groups in the same molecule, ambiguity exists about the type(s) of bonding to be expected. If a solution of $C_5H_5Mn(CO)_3$ in hexane is irradiated with ultraviolet light in the presence of acrylonitrile, it is possible to separate a complex with the formula $C_5H_5Mn(CO)_2CH_2{=}CHCN$ from the irradiation mixture by means of adsorption chromatography. The compound is relatively stable in the solid state but decomposes rather quickly in solution. Infrared and n.m.r. measurements show that the bonding to the substituted metal carbonyl utilizes the double bond of the acrylonitrile molecule. This is in interesting contrast to the bonding which occurs between acrylonitrile and manganese decacarbonyl in the complex $Mn_2(CO)_9CH_2CHCN$.[9]

Fischer and co-workers[2a] synthesized the complex $C_5H_5Mn(CO)C_4H_6$ by ultraviolet irradiation of a $C_5H_5Mn(CO)_3$–butadiene mixture. In this complex both π-bonding sites of butadiene are utilized. Indeed, irradiation of the $C_5H_5Mn(CO)_3$–butadiene mixture with a G.E. AH6 lamp for 3 hr. produced the same chelate complex, $C_5H_5Mn(CO)C_4H_6$, observed by Fischer and co-workers.[2a] However, irradiation under the same conditions, but for 30 min. only, yielded exclusively the complex $C_5H_5Mn(CO)_2C_4H_6$, in which only one of the π-bonding sites of butadiene has been utilized. This complex is an orange oil which decomposes slowly even under dry nitrogen into a compound whose formula is $[C_5H_5Mn(CO)_2]_2C_4H_6$. We believe this compound is the first known manganese metal carbonyl complex in which butadiene acts as a bridging ligand. Details of the preparations follow.

Experimental

(A) $C_5H_5Mn(CO)_2CH_2CHCN$ (I).—Cyclopentadienylmanganese tricarbonyl (500 mg., 2.56 mmoles) and 5 ml. (75 mmoles) of acrylonitrile were dissolved in 200 ml. of *n*-hexane. The solution was then exposed to ultraviolet radiation from a Hanovia Quartz burner (Type S-100) for 6 hr. in a reaction tube cooled by water. Purified nitrogen was bubbled through the solution before and during the irradiation. After 6 hr. the reaction mixture was filtered through a frit to remove small amounts of solid residue which appeared during the irradiation. The solvent was then removed by vacuum distillation. The residue was dissolved in a minimum amount of methanol (about 3–4 ml.) and adsorbed on an aluminum oxide column 10 cm. long and 1 cm. in diameter. The compounds were eluted with *n*-hexane. Elution time for the starting material, $C_5H_5Mn(CO)_3$, was very short but was approximately 4 hr. for the acrylonitrile derivative.

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