Chemistry

V. A. Ginsburg, S. S. Dubov, A. N. Medvedev, L. L. Martynova,

1963

SovietRxiv

Abstract

Full Text

Chemistry

V. A. Ginsburg, S. S. Dubov, A. N. Medvedev, L. L. Martynova, B. I. Tetelbaum, M. N. Vasil' eva, A. Ya. Yakubovich

THE STRUCTURE OF ADDUCTS OF TRIFLUORONITROSOMETHANE WITH UNSATURATED COMPOUNDS AND THE MECHANISM OF THEIR FORMATION

(Presented by Academician I. L. Knunyants, 23 V 1963)

In studying the reaction of polyfluorinated nitrosoalkanes with unsaturated compounds, we previously established the formation of various adducts and copolymers ([1,2]). In recent years this reaction has been widely studied by many authors ([3]); however, its mechanism remains unproved ([4–6]).

A key to understanding it may be provided by our experiments on the disproportionation of trifluoronitrosomethane, which showed a pronounced tendency of polyfluoronitroso compounds toward oxidation-reduction transformations ([7]).

By the e.p.r. method it was established that this reaction proceeds with the formation of ion-radicals, whose origin may be represented by the following scheme:

$$\mathrm{CF_3NO + OH^{(-)} \rightleftarrows CF_3N{-}O^{(-)} \xrightarrow{-(e)} CF_3\dot{N} \rightarrow \underset{|}{\underset{OH}{\dot{O}OH}}\ \underset{|}{\underset{OH}{CF_3NO_2}} + H_2O;}$$

$$\mathrm{CF_3NO + (e) \rightarrow CF_3\dot{N}{-}O^{(-)};}$$

$$\mathrm{CF_3\dot{N}{-}O^{(-)} + CF_3NO \rightleftarrows CF_3\dot{N}{-}NCF_3 \xrightarrow{(+)H} CF_3N{=}NCF_3 + \dot{O}H}$$

$$\begin{array}{cc} \mathrm{O^{(-)}O} & \mathrm{O\cdot} \\ \uparrow & \uparrow \end{array}$$

It was also established that bases (hydroxyl ion, amines, phosphines) facilitate this interaction, which, however, also proceeds in their absence, in a medium

of hydrogen-containing solvents, owing to redistribution of electrons in the molecules of the nitroso compounds, apparently at the stage of a π-complex

$$3CF_3NO \xrightarrow{\text{association}} CF_3\overset{O}{\overset{\|}{N}}\cdots\overset{O}{\overset{\|}{N}}CF_3 \rightarrow CF_3\overset{O^{(-)}}{\overset{|}{N}}-\overset{O}{\overset{\uparrow}{N}}CF_3 + CF_3\overset{(+)}{N}=O$$

$$\uparrow$$

$$CF_3NO$$

The ion-radicals formed are stabilized by solvation, and their concentration in a medium of, for example, ether, hexane, or toluene is very high even at a temperature of -120°. One could expect participation of similar ion-radicals in transformations of trifluoronitrosomethane with fluoroolefins.

In studying, by the e.p.r. method, systems containing trifluoronitrosomethane and a series of polyfluoroolefins (CF_2=CF_2, CF_2=CFCl, CF_2=CH_2), we in all cases detected paramagnetic particles with concentrations reaching, at $-60^\circ \div -40^\circ$, values of 10^{16-17} per cm^3.

From analysis of the h.f.s. of the signal in the indicated systems it may be concluded that the principal free-radical particle in all the cases listed is the ion-radical

$$CF_3\dot{N}CF_2-\overset{(-)}{C}XY \quad (\text{where } X, Y = F, Cl, H)$$

$$\downarrow$$

$$O$$

or the telo-

meric ion-radical

$$CF_3N\underset{O}{\overset{\cdot}{C}}F_2CXY\left[N(CF_3)OCF_2CXY\right]_n N(CF_3)OCF_2\overset{(-)}{C}XY$$

Any biradical particles of the type

$$CF_3N\underset{O}{\overset{\cdot}{C}}F_2\dot{C}XY$$

are absent in the system in appreciable concentrations.

At elevated temperatures in the systems (CF_3NO—unsymmetrical fluoroolefin), the observed ESR signal is reversibly changed into another one, corresponding to an ion-radical formed when the reagents are combined in the reverse order—

$$\underset{O}{CF_3\dot{N}CXY} - \overset{(-)}{C}F_2.$$

It follows from the foregoing that initiation of the copolymerization of trifluoronitrosomethane with fluoroolefins occurs by the ion-radicals that arise and proceeds by an anionic mechanism.

The influence on this process of any radical particles does not change the character of the principal reaction, but may lead to its complication through interaction with CF_3NO or with ion-radicals that lead to polymerization (cf. ([11])).

The side process—the formation of oxazetidine derivatives—may be regarded as a consequence of oxidation of the primary ion-radicals (by a free molecule of the nitroso compound) and sufficiently rapid recombination:

$$\begin{array}{c} \overset{(-)}{CF_2}CXY \\ | \\ CF_3N \to O \end{array} \xrightarrow{-(e)} \begin{array}{c} CF_2{-}CXY \\ \\ N{-}O \end{array} \quad \begin{array}{c} | \\ | \end{array}$$

Of considerable interest is the reaction, investigated by us, of trifluoronitrosomethane with styrenes (styrene; α,β,β-trifluorostyrene). In this case, under conditions of elevated temperatures, the main products of the interaction proved to be solid colorless adducts, decomposing at temperatures $> 70^\circ$, of composition 1 mole of styrene to 2 moles of nitroso compound. On the basis of a number of chemical transformations, as well as investigation of their IR spectrum, ^{19}F NMR, and the high values found for the dipole moments (respectively, for the styrene and α,β,β-trifluorostyrene adducts: 4.5 D and 5.5 D), they may be assigned the structures A and B with semipolar bonds:

$$\begin{array}{c} C_6H_5CH{-}CH_2 \\ | \qquad \backslash O \text{ (A)} \\ CF_3N{-}N \\ \downarrow \quad | \\ O \quad CF_3 \end{array} \qquad \begin{array}{c} C_6H_5CF{-}CF_2 \\ | \quad | \\ CF_3N{-}NCF_3 \text{ (B)} \\ \downarrow \quad \downarrow \\ O \quad O \end{array}$$

$$\text{(A)} \xrightarrow{<70^\circ} CF_3NO + \begin{array}{c} C_6H_5CH{-}CH_2 \\ | \quad | \\ CF_3N{-}O \end{array} \qquad \text{(B)}$$

$$(B) \xrightarrow{\text{pyrolysis}} CH_2O + [C_6H_5CH{=}NCF_3] \rightarrow C_6H_5CHO + CO_2 + 3HF + NH_3$$

$$C_6H_5COF + CF_3N{=}CF_2$$

$$(B) \xrightarrow{>70^\circ} CF_3NO + \begin{array}{c} C_6H_5CF{-}CF_2 \\ | \quad\quad | \\ O{-}NCF_3 \end{array} \quad (G)$$

$$(G) \begin{array}{c} \xrightarrow{\text{pyrolysis}} \\ \xrightarrow[H_2O]{HJ} \end{array} \begin{array}{c} C_6H_5COF + CF_3N{=}CF_2 \\ C_6H_5COCONHCF_3 \end{array}$$

(the dipole moments of the four-membered adducts B and G correspond to 3.0 D).

Products B and G are the main ones in the reaction of trifluoronitrosomethane with styrenes at temperatures $> 70^\circ$.

In the EPR spectra, recorded both during the formation of these adducts (A and B) and during their thermal destruction, paramagnetic particles are found with parameters practically coinciding both for styrene and for

Table 1

Properties of the synthesized compounds

No.	Compound	b.p. (m.p.), °C	d_{20}^{20}	n_D^{20}	Mol. wt.
1	$C_2F_4 \cdot 2CF_3NO \cdot 2(C_2H_5)_2O$	42(2)	1.323	1.5810	332(in benzene)
2	$(C_2F_4 \cdot CF_3NO)_2$	98(760)	1.713	[1]	426(in Freon 112)
3	$(C_2F_4 \cdot CF_3NO)_3$	38(2)	1.916	[1]	575(in Freon 112)
4	$(C_2F_4 \cdot CF_3NO)_4$	62(2)	1.948	[1]	840(in Freon 112)
5	$(C_2H_4 \cdot CF_3NO)_5$	95(2)	1.980	[1]	985(in Freon 112)
6	$C_6H_5CH-\overset{\frown}{CH_2}ONCF_3$	90(5)	1.250	1.4730	198(in benzene)
7	$C_6H_5CF-\overset{\frown}{CF_2}NCF_3)O$	70(75)	1.401	1.4065	251(in benzene)

No.	Compound	b.p. (m.p.), °C	d_{20}^{20}	n_D^{20}	Mol. wt.
8	$C_6H_5COCONHCF_3$	(62)[2]	–	–	
9	$HO_2CCONHCF_3$	(125)[3]	–	–	
10	$C_6H_5CH-CH_2$ | CF_3N-N/O | O	(72)	–	–	207(in benzene)
11	$C_6H_5CF-CF_2$ | $CF_3N-N-CF_3$ | O–O	(76)	–	–	352(in benzene)
12	$CF_3N(OH)CH=C(CH_3)CO_2CH_3$	99(5)	1.338	1.6150	362(in benzene)
13	$CF_3N(OH)CHBrC(CH_3)CO_2CH_3$	(52)	1.487	1.4689	
14	$CF_3N=CClCCl(CH_3)CO_2CH_3$[3]	(62)	1.457	1.4141	210(in benzene)
15	$H_2NCOCCl(CH_3)CO_2CH_3$[4]	(200)	–	–	
16	$CF_3N(OH)CH=C(CH_3)CO_2CH_3$	125(10)	1.458	1.4017	191(in benzene)
17	$CF_3N(OH)CH=C(CH_3)CO_2H$	(100)	–	–	
18	$CF_3N(OH)CH=C(CH_3)OCOCH_3$[5]	60(2)	1.400	1.3800	213(in benzene)
19	$CF_3N(OH)CHBrC(CH_3)OCOCH_3$	84(2)	1.800	1.4423	343
20	$CF_3N(OH)CH_2CH(CH_3)NH-C_6H_3(NO_2)_2$	(290)	–	–	–

Notes. [1] Refractive index below the lower limit of the Abbe refractometer. [2] Obtained by reduction of perfor. N-methyl oxazetidine with aqueous hydroiodic acid. [3] Obtained from $N_2 + PCl_5$. [4] Obtained from N^{14} + aqueous ammonia. [5] Along with the indicated product, its oligomers are formed, with b.p. 80-90/2°; $d_{20}^{20} = 1.445$; $n_D^{20} = 1.3860$; b.p. 110/2°; $d_{20}^{20} = 1.487$; $n_D^{20} = 1.3385$, and a crystalline adduct with m.p. 168°, corresponding to the indicated composition.

for α, β, β-trifluorostyrene.* They may be assigned to ion-radicals of the structure:

$$\begin{array}{c} C_6H_5CX-CX_2 \\ | \\ O \leftarrow NCF_3 \\ | \\ O \leftarrow NCF_3 \end{array} \quad \text{or} \quad \begin{array}{c} C_6H_5CXCX_2 \\ | \\ O \leftarrow NCF_3 \\ | \\ O \leftarrow NCF_3, \end{array} \quad \text{where } X = H, F$$

It is not excluded that in other cases as well, in the interaction of unsaturated compounds with nitrosoalkanes at low temperatures, analogous

* On heating these systems to room temperature, as in the CF_3NO–hydrogen-containing solvent systems, the appearance of doublets at all lines of the e.p.r.

signal is observed, which may be explained by association of the arising ion-radicals through hydrogen-bonding type interactions.

intermediate associates containing two CF_3NO groups. To stabilize such systems, an additional negative charge is required, neutralizing the effect of the electron-withdrawing R_F groups (cf. dimers of nonfluorinated nitrosoalkanes [10]). In the case of styrenes these intermediate complexes are sufficiently stable and cyclize without a change in composition.

For aliphatic fluoroolefins such products are only slightly stable, although under known conditions they also can be isolated (the etherate of the adduct $C_2F_4 \cdot 2CF_3NO$—see Table 1).

In studying the reaction of trifluoronitrosomethane with other unsaturated compounds not containing fluorine, such as acrylates and vinyl acetate, it was similarly established that the interaction also proceeds according to an ion-radical scheme.

However, in this case the reaction is complicated and leads to the formation of a series of undefined low-molecular-weight (cf. [8,9]) and polymeric substances (see Table 1), evidently according to a scheme such as:

$$CF_3NO + CH_2 = C(CH_3)CO_2CH_3 \rightarrow [CF_3\dot{N}CH_2C^{(-)}(CH_3)CO_2CH_3]^+$$

$$\downarrow$$

$$O$$

$$\xrightarrow[\text{migration of a hydrogen atom}]{-(e)} CF_3N{-}CH{=}C(CH_3)CO_2CH_3$$

$$|$$

$$OH$$

Received
17 V 1963

CITED LITERATURE

[1] A. Ya. Yakubovich, V. A. Shpanskii, A. L. Lemke, DAN, **96**, No. 4, 774 (1954).
[2] S. P. Makarov, V. A. Shpanskii, V. A. Ginsburg et al., DAN, **142**, No. 3, 596 (1962).
[3] J. M. Ontermoso, Rubber Chem. and Techn., No. 5, 1521 (1961).
[4] D. A. Barr, R. H. Haszeldine, J. Chem. Soc., **1955**, 1881; **1956**, 3416.
[5] G. H. Crawford, J. Polym. Sci., **45**, No. 145, 261 (1960).
[6] D. A. Barr, R. H. Haszeldine, C. J. Willis, J. Chem. Soc., **1961**, 1351.
[7] A. Ya. Yakubovich, V. A. Ginsburg et al., DAN, **140**, No. 6, 1352 (1961).

[8] G. N. Burkhardt, A. Lapworth, J. Walkden, J. Chem. Soc., **127**, 2458, 1742 (1925).
[9] C. K. Ingold et al., J. Chem. Soc., **125**, 93, 1456 (1924).
[10] J. Batt, B. G. Gowenlock, J. Chem. Soc., **1960**, 376.
[11] G. H. Crawford, D. E. Rice, B. F. Landrum, J. Polym. Sci., Part A, **1**, 565 (1963).

Note: Figure translations are in progress. See original paper for figures.