tive rate at each position is therefore 600 × 5 = 3000; and the rate for *p*-xylene relative to that for benzene is 4 × 3000/6 = 2000. Similarly, inasmuch as the single available position in pentamethylbenzene is influenced by one para, two meta, and two ortho methyls, the rate of chlorination of pentamethylbenzene relative to that of benzene is $870 \times 5 \times 5 \times 600 \times 600/6 = 1.3 \times 10^9$. Such calculated relative rates are compiled in Table I, together with available experimental values[1] for chlorination or bromination. The agreement between the calculated and the experimental values, which is good in view of the 350,000-fold range, inspires considerable confidence in the five values for which experimental confirmation is at present unavailable.

A product of relative rates as calculated above is mathematically related to a sum of activation energy differences calculated from Arrhenius-type equations for the individual rate constants

$$k = Ae^{-E/RT}$$

For

$$k_i/k = (A_i/A)e^{(E-E_i)/RT}$$

and

$$\Sigma(E - E_i) = \Sigma RT \ln (k_i/k) - \Sigma RT \ln (A_i/A) = RT \ln \Pi(k_i/k) - RT \ln \Pi(A_i/A)$$

If the several A terms are equal,[4] the relationship simplifies to

$$\Sigma(E - E_i) = RT \ln \Pi(k_i/k)$$

According to the theory of absolute reaction rates[5]

$$k = (KT/h)e^{-F/RT}$$

where K = Boltzmann constant, h = Planck constant, and F = difference in free energy between initial and activated states, or "activation free energy." Consequently, without any assumption of constancy for an A term, or "frequency factor"[5]

$$k_i/k = e^{(F-F_i)/RT}$$

and

$$\Sigma(F - F_i) = RT \ln \Pi(k_i/k)$$

so that a product of relative rates is simply related to a sum of activation free energy differences.

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[4] *Cf.* Bradfield and Jones, *J. Chem. Soc.*, 1006, 3073 (1928); *Trans. Faraday Soc.*, **37**, 737 (1941).

[5] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

BARTLESVILLE, OKLAHOMA RECEIVED NOVEMBER 28, 1947

Liquid Nitrosyl Chloride as an Ionizing Solvent

BY ANTON B. BURG AND GEORGE W. CAMPBELL, JR.[1]

Liquid nitrosyl chloride is expected to be a fairly effective ionizing solvent, for its dielectric constant (18.2 at 12°)[1a] is comparable to that of liquid ammonia. The acid–base system would be defined by the neutralization equation $NO^+ + Cl^- \rightarrow NOCl$. As in the analogous case of carbonyl chloride,[2] the chloride ion should not be appreciably solvated, for the electronic structure of NOCl (resonance between $:\underset{..}{O}{=}\underset{..}{N}{}^+Cl^-$ and $:\underset{..}{O}{=}\underset{..}{N}{-}\underset{..}{\ddot{Cl}}:$)[1,3] will not be affected by an electron-donor so weak as chloride. In agreement with this prediction, potassium chloride is insoluble in liquid nitrosyl chloride, contributing no conductance effect.

The nitrosyl ion, on the other hand, should be solvated very strongly, on account of the resonance structures $\left[:\underset{..}{O}{=}\underset{..}{N}{-}\underset{..}{\ddot{Cl}}{-}\underset{..}{N}{=}\underset{..}{O}:\right]^+$, $\left[:\underset{..}{O}{=}\underset{..}{N}{-}\underset{..}{\ddot{Cl}}:\right]\ :\overset{+}{N}{\equiv}O:$, and $:O{\equiv}\overset{+}{N}:\ \left[:\underset{..}{\ddot{Cl}}{-}\underset{..}{N}{=}\underset{..}{O}:\right]$. Hence it is expected that nitrosyl salts, many of which have been recognized,[4] should be soluble in liquid nitrosyl chloride, with high electrical conductance.

Experimental Results.—These ideas have been tested in a preliminary investigation of the electrical conductance of solutions of typical nitrosyl salts in liquid nitrosyl chloride. The mononitrosyl salts $NOAlCl_4$, $NOFeCl_4$ and $NOSbCl_6$ are readily soluble strong electrolytes, as demanded by the theory (see Table I). The solvation is indicated by the reaction $NOAlCl_4(s) + NOCl(g) \leftrightarrows NOAlCl_4{\cdot}NOCl(s)$, recently discovered in our laboratories by Donald E. McKenzie. The dissociation pressure of the product is approximately 240 mm. at 0°.

Less favorable results were obtained with $(NO)_2SnCl_6$, $(NO)_2TiCl_6$, and $(NOSO_4H)$, all of which appeared quite insoluble and non-conducting. Dinitrosyl pyrosulfate, $(NO)_2S_2O_7$,[5] showed a slight conductance which very slowly passed through a maximum (see Table II). Sulfuric acid was inert.

The inert character of potassium chloride was not changed by an "acid" solution of nitrosyl chloroantimonate, which, by analogy with carbonyl "acids" in carbonyl chloride, should have dissolved it. The reason might be a protective coating of $KSbCl_6$.

In an attempt to establish chloride ions in liquid NOCl, the base-action of water was tried. However, the water only dissolved without conductance and was recovered by evaporating the nitrosyl chloride. The usual hydrolysis reaction $H_2O + 2NOCl \rightarrow NO + NO_2 + 2HCl$ is slow at room temperature and the products are non-conducting in nitrosyl chloride.

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[1] This note is based upon a thesis submitted by George W. Campbell, Jr., to the Graduate Faculty of the University of Southern California, in partial fulfillment of the requirements for the degree of Master of Science, June, 1947.

[1a] Ketelaar, *Rec. trav. chim.*, **62**, 289 (1943).

[2] (a) Germann and Gagos, *J. Phys. Chem.*, **28**, 965 (1924); (b) Germann and Timpany, *ibid.*, **29**, 1423 (1925); (c) Germann and Birosel, *ibid.*, **29**, 1469 (1925); (d) Germann, THIS JOURNAL, **47**, 2465 (1925); (e) Germann and Timpany, *ibid.*, **47**, 2275 (1925).

[3] Ketelaar and Palmer, *ibid.*, **59**, 2629 (1937).

[4] (a) Willke-Dörfurt and Balz, *Z. anorg. allgem. Chem.*, **159**, 219 (1927); (b) Gall and Mengdehl, *Ber.*, **60B**, 86 (1927); (c) Rheinboldt and Wasserfuhr, *ibid.*, **60B**, 732 (1927); (d) Angus and Leckie, *Proc. Roy. Soc.* (*London*), **A150**, 615 (1935); (e) Klingenberg, *Rec. trav. chim.*, **56**, 749 (1937).

[5] Jones, Price and Webb, *J. Chem. Soc.*, **135**, 312 (1929).

Methods and Numerical Results.—All reagents were prepared and handled with complete exclusion of moisture. The nitrosyl chloride was prepared by the usual reaction $NOSO_4H + HCl \rightarrow H_2SO_4 + NOCl$, and purified by means of a helix-packed column. With electrodes of bright platinum wire 1 mm. thick, having 12 mm. exposed length, and 6 mm. apart, polarization effects caused a 15% uncertainty in the evaluation of the cell constant (0.78) by reference to aqueous KCl, but the various NOCl solutions gave results consistent to 1%. These results accordingly are presented in Tables I and II for purposes of comparison.

TABLE I

CONDUCTANCES IN LIQUID NITROSYL CHLORIDE

Solute	Molarity	Temp., °C.	Spec. cond., mhos.	Molar cond.
$NOAlCl_4$	0.098	−20	1.17×10^{-2}	119
$NOFeCl_4$	.0099	−20	1.34×10^{-3}	136
$NOFeCl_4$	.0094	−21	1.26×10^{-3}	134
$NOFeCl_4$	.0094	−44	1.00×10^{-3}	106
$NOSbCl_6$	.140	−20	2.35×10^{-2}	168
$NOSbCl_6$	.140	−44	2.20×10^{-2}	157
NOCl	Pure	−20	2.88×10^{-6}	...

TABLE II

CONDUCTANCES OF $(NO)_2S_2O_7$ (SATD. IN NOCl) AT −20°

Time, hr.	0	0.75	2	15	46
Spec. cond. $\times 10^6$	4.95	25.0	48.8	23.8	14.7

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RECEIVED DECEMBER 11, 1947

The Effect of Sulfur Fluorides on the Viscosity of Sulfur

BY R. FANELLI

Recently, it was shown,[1,3] that the halogens, chlorine, bromine, iodine and also hydrogen sulfide and hydrogen persulfides, even when present in minute amounts, reduce the viscosity of sulfur above 160°. The degree of effectiveness decreased, with respect to the halogens, in the order shown. It was also indicated that the increasing viscosity of pure sulfur with rise in temperature might be due to polymerization of sulfur into long straight chains and that reduction of the viscosity was due to the rupture of these chains by the halogens which take up terminal positions of the segments. For example, in the case of chlorine added in the form of sulfur chloride we have

$$S_n(\text{chain}) + S_2Cl_2 \longrightarrow Cl\text{–}S\text{–}S\text{–}S \cdots S\text{–}S\text{–}SCl \text{ and/or } Cl\text{–}S\text{–}S\text{–}S \cdots S\text{–}S\text{–}S.$$

Sulfur mixtures containing 2% chlorine give viscosities under 15 centipoises throughout the entire liquid range, 115–445°. This is in sharp contrast with the maximum viscosity of pure sulfur, 93,200 centipoises, at 186–188°.

Fluorine was not tried in the earlier experiments because of the difficulty in obtaining this element. It was assumed, however, that because of its position in the halogen group it would be much more effective than chlorine. Recently, sulfur hexafluoride became available commercially and it was used in the same manner as sulfur chloride. Because of its high thermal stability, sulfur hexafluoride, if effective, would be an attractive reagent for reducing the viscosity of sulfur.

Experimental

Quantitative data were not obtained as the nature of the work was exploratory. The effect of the sulfur fluorides was determined by visual comparison of the fluidity of the treated sulfur with that of pure sulfur[2] which at 180–195° shows very little or no flow in the space of a few minutes.

Sulfur hexafluoride was bubbled for five and one-half hours through pure sulfur heated to 310° during which period little, if any, decrease in viscosity was noted. On cooling from 310 to 194° with the gas still bubbling through, the sulfur gelled indicating that the sulfur hexafluoride was comparatively ineffective in reducing the viscosity of sulfur. Apparently the stability and inertness of the hexafluoride is such that its reaction with the long sulfur chains is negligible under the conditions of the experiment.

The direct fluorination of sulfur gives in addition to the hexafluoride much smaller and variable concentrations of SF_4, S_2F_2, and (about 1%) S_2F_{10}. As revealed by Schumb,[4] these lower fluorides are removed before the purified hexafluoride is compressed into the cylinders. These lower fluorides are less stable and more reactive than the hexafluoride and might react with the long sulfur chains to appreciably reduce the viscosity.

The effect of the gases SF_4 and S_2F_2 was determined by heating in an electric furnace mixtures of pure sulfur with metallic fluorides in rotating, sealed, heavy-walled Pyrex tubes (free volume about 15 cc.). For the preparation of SF_4 the following reaction, reported to yield this compound,[4–7] was employed

$$4CoF_3 + S \longrightarrow 4CoF_2 + SF_4$$

Under the conditions of this experiment, probably some of the cobaltous fluoride was converted to sulfide. For the formation of S_2F_2 two reactions reported to yield this halide[6,7] were tried

$$2HgF + 3S \longrightarrow Hg_2S + S_2F_2$$
$$2AgF + 3S \longrightarrow Ag_2S + S_2F_2$$

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[1] R. F. Bacon and R. Fanelli, THIS JOURNAL, **65**, 639 (1943).

[2] R. F. Bacon and R. Fanelli, *Ind. Eng. Chem.*, **34**, 1043 (1942).

[3] R. Fanelli, *ibid.*, **38**, 39 (1946).

[4] W. C. Schumb, *ibid.*, **39**, 421 (1947).

[5] J. Fischer and J. Werner, *Z. angew. Chem.*, **42**, 810 (1929).

[6] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X, Longmans, Green & Company, London, England, 1930, p. 631.

[7] Don M. Yost and Horace Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, pp. 295 and 299.