Heats of Formation of Uranium Oxides

Reaction	ΔH kcal. Mixter's values Peroxide bomb	ΔH kcal. Mixter's values Oxygen bomb	ΔH kcal. This paper oxygen bomb
$3U + 4O_2 = U_3O_8$	−895.5	−845.2	−853.5 ± 1.6
$3UO_2 + O_2 = U_3O_8$	− 86.4	− 75.3	− 76.01 ± 0.09
$U + O_2 = UO_2$	−269.7	−256.6	−259.2 ± 0.6

with O_2 and of U, UO_2 and U_3O_8 with Na_2O_2. The values he obtained with oxygen do not agree with the values he obtained with sodium peroxide. Our values are in fair agreement with his oxygen values as can be seen in the adjoining table:

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NOTES

Some Inorganic Reactions of Nitryl Chloride

By Harry H. Batey and Harry H. Sisler

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The improvement in methods for the synthesis of nitryl chloride, which has made possible its convenient preparation in the laboratory, has resulted in a considerable increase in interest in its reactions and particularly in its possible use as a reagent in organic synthesis. By analogy with nitrosyl chloride it was at first considered to be a possible source of the nitronium (NO_2^+) group and of negative chlorine. Schmiesser,[1] however has reported that at very low temperatures in the liquid or solid phase, nitryl chloride reacts with ammonia to yield chloramine and ammonium nitrite. This would indicate that nitryl chloride behaves as a source of positive chlorine and negative nitrite. Schmiesser, however, gives very little information concerning his experiments. We were, therefore, interested in carrying out the reaction of nitryl chloride with ammonia under a variety of conditions, and further to observe the behavior of nitryl chloride toward a variety of other reagents which might give some indication concerning its polar characteristics.

Experimental

Preparation of Nitryl Chloride.—The method used was that of Dachlauer[2] as modified by Shechter and Kaplan.[3] This method involves the reaction, in the absence of moisture, of anhydrous nitric acid with chlorosulfuric acid. To the anhydrous nitric acid (1.4 moles), cooled to −0.5°, was added in a dropwise manner with vigorous stirring over a period of two hours, 1.4 moles of chlorosulfuric acid. Nitryl chloride distilled out of the mixture and condensed in at −80°. The receiver was disconnected as soon as the addition of chlorosulfuric acid was complete. A yield of 1.1 moles of NO_2Cl was obtained as a pale yellow liquid freezing at −145° (lit. −145°).

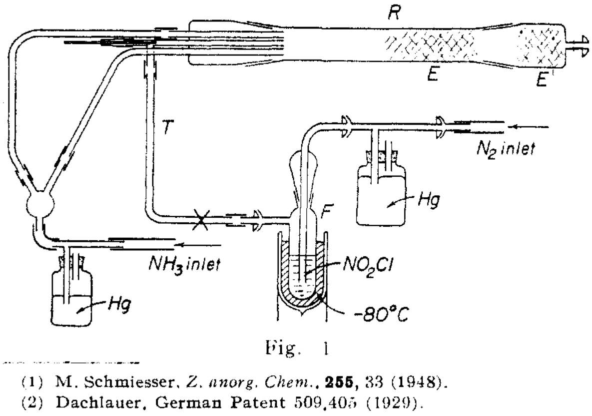

Fig. 1

Reaction of Nitryl Chloride with Ammonia in the Liquid Phase.—The addition of liquid nitryl chloride to liquid ammonia even at −75° results in a very violent reaction. The reaction takes place somewhat less violently but still very vigorously when gaseous ammonia, diluted with nitrogen gas, is passed into dilute solutions of nitryl chloride in inert solvents such as carbon tetrachloride, diethyl ether or petroleum ether. In all these cases the products of the reaction include chloramine, hydrazine, ammonium nitrite and ammonium chloride. In no case was an appreciable amount of nitrate found.

Reaction of Nitryl Chloride with Ammonia in the Gas Phase.—In order to reduce the vigor of the reaction the mixing of nitryl chloride (diluted with nitrogen) with an excess of ammonia was carried out in the gaseous state using the apparatus shown in Fig. 1. The outlet from E′ was connected to a series of three traps, cooled to −80°. The residual gas was finally bubbled into water. Nitryl chloride contained in bubbler F was entrained in a stream of nitrogen gas and passed into reactor R (60 cm. long × 4.5 cm. in diameter) at 25° where it was mixed with a large excess of gaseous ammonia. The reaction which occurred was immediate but was not violent and there was no noticeable heating of the reaction chamber. The effluent gases gave strong tests for the presence of chloramine. The white solid formed was filtered out by the glass wool plugs at E and E′. Gases from the reactor tube were condensed at −80° in the traps and the water bubbler was used to remove the last traces of chlorine-containing substances.

The solid contents of the reactor were dissolved in water and analyzed for hydrazine and chloride, and tested qualitatively for nitrite and nitrate. No hydrazine or nitrate was ever detected in this portion of the system, but the presence of an abundance of nitrite was indicated. In a series of experiments carried out in this manner amounts of chloride corresponding to from 10 to 15% of the nitryl chloride were found in the glass wool plugs in the reactor. Mattair and Sisler[4] had found, in the reaction of chlorine with ammonia to produce chloramine in a similar reactor that up to about 10% of the chloramine produced by the chlorine–ammonia reaction decomposes to ammonium chloride in the reactor tube. Assuming that a similar proportion of chloramine might decompose in the nitryl chloride–ammonia reaction, we may conclude that the reaction of nitryl chloride and ammonia in the gaseous phase proceeds quantitatively to yield chloramine and ammonium nitrite; and that the chloride found in the reactor results from the secondary decomposition of a small portion of the chloramine so produced.

The liquid ammonia solutions of chloramine in the traps were allowed to stand at −75° overnight and then to evaporate. White solid residues composed of a mixture of hydra-

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(1) M. Schmiesser, *Z. anorg. Chem.*, **255**, 33 (1948).

(2) Dachlauer, German Patent 509,405 (1929).

(3) Private communication, 1948.

(4) R. Mattair and J. Sisler, This Journal, **73**, 1619 (1951).

TABLE I

REACTION OF NO_2Cl WITH SOME LEWIS ACIDS

Reactant	Conditions	Results	Products
$SnCl_4$	Excess NO_2Cl, −75°	No reaction	
$SnBr_4$	Excess NO_2Cl, −75°	Vigorous reaction, Br_2 evolved	$(NO)_2SnCl_6$[a] + oxychlorides of tin + N_2O_4
SnI_4	Excess NO_2Cl, −75°	Vigorous reaction, I_2 evolved	
BF_3	Excess NO_2Cl, −75°	No reaction	(N_2O_4 impurity in NO_2Cl forms some $N_2O_4 \cdot 2BF_3$—a white crystalline solid)
PCl_3	Excess PCl_3; NO_2Cl distilled in at −75°	Exothermic reaction	PCl_5, $POCl_3$, NOCl, N_2O_4
SO_3	Liq. SO_3 added to excess NO_2Cl at −75°	Violent reaction, voluminous white precipitate	$NO_2Cl \cdot 2SO_3$[b]—presumably $NO_2(ClS_2O_6)$ nitronium chlorodisulfate
$SiCl_4$	Excess NO_2Cl; −75°	No reaction	Residue contained no Cl^-, NO_3^-, or NO_2^-
WO_2	NO_2Cl refluxed over WO_3 for 12 hours	No reaction	Residue contained no Cl^-, NO_3^-, or NO_2^-
MoO_3	NO_2Cl refluxed over MoO_3 for 12 hours	No reaction	Residue contained no Cl^-, NO_3^-, or NO_2^-
I_2O_5	NO_2Cl refluxed over I_2O_5 for 12 hours	No reaction	Residue contained no Cl^-, NO_3^-, or NO_2^-
SO_2	Equal volumes of liquid SO_2 and NO_2Cl refluxed for 36 hours	Miscible. No apparent reaction	No residue

[a] Bright, yellow, solid sublimes above 150°. *Anal.* Calcd.: Cl, 54.31; Sn, 30.37. Found: Cl, 50.88; Sn, 33.68. Product thus is impure, but agrees with properties reported for $(NO)_2SnCl_6$ by H. Reinbolt and R. Wasserfuhr, *Ber.*, **60B**, 732 (1927). [b] *Anal.* Calcd. for $NO_2(ClS_2O_6)$: Cl, 14.67; S, 26.54; N, 5.79. Found: Cl, 12.90; S, 26.65; N, 5.48. Product was so susceptible to hydrolysis that some chlorine was lost as HCl during analysis. Melted at about 120° and crystallized as long sharp needles. Exceedingly hygroscopic. Fumes even in the presence of phosphoric anhydride.

zine monohydrochloride and ammonium chloride were obtained. Yields of hydrazine monohydrochloride amounting to 15% of theoretical based on the nitryl chloride used were obtained. As already shown in a previous publication[4] the yields can be increased. We were, however, interested here in the primary reaction of the nitryl chloride. The above results are in agreement with those obtained by Schmiesser and with the equations

$$NO_2Cl + 2NH_3 \longrightarrow NH_4NO_2 + ClNH_2$$
$$ClNH_2 + 2NH_3 \longrightarrow N_2H_4 + NH_4Cl$$

Qualitative results obtained for the liquid phase reaction likewise fit this picture.

Reaction of Nitryl Chloride with A Series of Lewis Acids.—A series of qualitative or semi-quantitative experiments were carried out in which the behavior of nitryl chloride toward various Lewis acids most of which might be expected to coördinate negative chlorine was observed. The results of these experiments are summarized in Table I.

These results indicate that, with the exception of sulfur trioxide, there is no reaction with these Lewis acids except where oxidation–reduction processes occur.

Reaction of Nitryl Chloride with Metals.—In order to determine whether NO_2 or Cl can be readily displaced from nitryl chloride by metals in such reactions as

$$2NO_2Cl + M \longrightarrow MCl_2 + N_2O_4$$

or

$$2NO_2Cl + M \longrightarrow M(NO_2)_2 + Cl_2$$

a series of tests with a variety of metals was carried out. Samples of chemically pure zinc, mercury, bismuth, copper, magnesium, iron, aluminum and tin were added to 10-ml. portions of nitryl chloride and kept at −30° in sealed tubes for six hours. At the end of this time only mercury showed any evidence of having reacted. The samples were then cooled to −75° at which temperature they were held for an additional 36 hours. At the end of this time the nitryl chloride was allowed to boil off. The metal specimens and their containers were thoroughly washed and the wash liquid tested for metal cation, nitrate ion, nitrite ion and chloride ion.

With copper, magnesium, iron, aluminum and tin there was no indication of reaction with nitryl chloride.

With mercury, bismuth and zinc, however, the aqueous wash liquid gave strong tests for metal cations, nitrite and chloride. In the reaction with mercury a thin film of gray solid formed on the mercury surface stopping the reaction. The reaction could be started again by shaking the mercury so as to expose a fresh metal surface. The reactions with zinc and bismuth were much less apparent and proceeded very slowly under the conditions of the experiment. The reactions of zinc, bismuth and mercury with nitryl chloride yield a mixture of the metal nitrites and chlorides and in the case of mercury, of mercurous and mercuric salts. The reactions which occur are probably

$$2Bi + 3NO_2Cl \longrightarrow BiCl_3 + Bi(NO_2)_3$$
$$2Zn + 2NO_2Cl \longrightarrow ZnCl_2 + Zn(NO_2)_2$$
$$2Hg + 2NO_2Cl \longrightarrow HgCl_2 + Hg(NO_2)_2$$
$$4Hg + 2NO_2Cl \longrightarrow Hg_2Cl_2 + Hg(NO_2)_2$$

Discussion

The results reported above indicate that the nitrogen to chlorine bond in nitryl chloride is not so polarized as to act as a source of negative chlorine except toward exceedingly strong electron acceptors such as sulfur trioxide. This is supported strongly by the facts that the reaction with ammonia yields chloramine and ammonium nitrite rather than nitramide and ammonium chloride, and that nitryl chloride does not react with tin tetrachloride or with boron trifluoride. The reactions with tin tetrabromide, tin tetraiodide and phosphorus trichloride indicate that nitryl chloride can act as an oxidizing agent either by losing oxygen and forming nitrosyl chloride or by losing chlorine and forming dinitrogen tetroxide. This is in accord with the structure O_2N–Cl.

Schmiesser[2] has stated that the formation of chloramine and of hypochlorite by the reactions of nitryl chloride with liquid ammonia and aqueous sodium hydroxide, respectively, indicates that nitryl chloride is in reality nitrosyl hypochlorite with the structure

$$O{=}N{-}O{-}Cl$$

Such an assumption is clearly unnecessary for the ammonolysis of nitryl chloride may yield either nitramide or chloramine depending upon the polarity of the N–Cl bond, as represented

$$\begin{matrix} \overset{-}{O_2N} & \overset{+}{Cl} \\ \overset{+}{H} & \overset{-}{NH_2} \end{matrix} \longrightarrow H_2N{-}Cl \qquad \begin{matrix} \overset{-}{Cl} & \overset{+}{NO_2} \\ \overset{+}{H} & \overset{-}{NH_2} \end{matrix} \longrightarrow H_2N{-}NO_2$$

The chlorine in nitrosyl chloride is clearly negative in polarity. The addition of a second oxygen atom to the nitrogen atom in nitryl chloride has either greatly reduced this negative polarity or actually changed it to positive.

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Preparation of Substituted Bis-phenols

BY DAVID J. BEAVER AND PAUL J. STOFFEL

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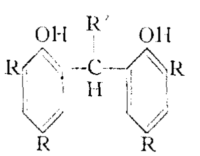
Since the original synthesis[1] of Baeyer, numerous papers on phenol–aldehyde condensations have appeared in the literature.[2] More recently, an increasing interest has been shown by various investigators of this type compound as intermediates for phenolic resins,[3] as antioxidants for wax,[4] as rubber chemicals,[5] as bacteriocides,[6] and as fungicides.[7]

The present work was directed toward the preparation of bis-phenols of the general formulas



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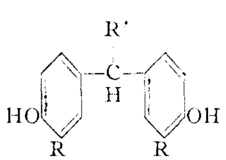

in which R = alkyl, aryl or chlorine and R′ = alkyl or aryl, for use as rubber antioxidants and bacteriostatic agents. A search of the literature revealed a surprisingly small number of bis-phenols other than derivatives of phenol and the cresols with formaldehyde[3] and chloral.[6]

This paper describes the preparation of 35 polyalkylated and chlorinated phenol–aldehyde condensation products not reported previously. They are white crystalline compounds in all cases except 4,4′-(*p*-hydroxybenzylidene)-bis-(6-*t*-butyl-*m*-cresol), #9, which is lemon yellow.

The wide applicability and versatility of the described procedures can readily be seen from the following tables. The reaction time, as given, was the point at which resin formation was observed and the batch quenched with the designated precipitant. The reaction times are, therefore, not true measures of the reaction rates but they do definitely indicate the wide variations observed by changing the structure of the phenols and aldehydes. Since the formation of bis-phenol and resin is a competitive reaction, the low yields can be attributed to either insufficient reaction time for bis-phenol formation or, conversely, not quenching quickly enough to prevent the bis-phenols formed from condensing further to resinous products. The reported yields have no quantitative significance, since in most cases the figures given are the results of a single run.

The compounds described in Table I are 4,4′-alkylidene or arylidene bis-phenols since they do not form nitroso derivatives as does the unreacted 6-*t*-butyl-*m*-cresol. The specific preference for 4,4′-linkage in ortho–para competition is probably a result of partial steric hindrance,[8] although condensation in the ortho position does occur, if the para position is occupied. Examples are given in compounds 20, 28 and 34 in which 4,6-di-*t*-butyl-*m*-cresol is condensed in the one available ortho position with three different aldehydes.

TABLE I

BIS-PHENOLS FROM 6-*t*-BUTYL-*m*-CRESOL[a]

No.	Aldehyde	Precipitant[b]	Time, hr.	M.p., °C.	Yield, %	Recrystallizing solvent	Empirical formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
1	Formaldehyde	1	2	178.7–179.2	39.0	Heptane	$C_{23}H_{32}O_2$	81.12	81.01	9.47	9.53		
2	Acetaldehyde	1	1/4	201.1–201.5	87.0	Heptane	$C_{24}H_{34}O_2$	81.31	80.93	9.67	9.99		
3	Chloroacetaldehyde	1	1/4	228.5–229.5	45.9	Heptane	$C_{24}H_{33}ClO_2$	74.09	73.93	8.55	8.58	9.12	8.95
4	Propionaldehyde	1	4	190.0–190.4	43.4	Heptane	$C_{25}H_{36}O_2$	81.48	81.29	9.85	9.92		
5	Butyraldehyde	2	8	210.0–210.7	62.8	Heptane	$C_{26}H_{38}O_2$	81.64	81.91	10.01	10.23		
6	Isobutyraldehyde	1	24	229.8–230.7	50.8	Heptane	$C_{26}H_{38}O_2$	81.64	81.47	10.01	9.94		
7	Heptaldehyde	2	12	160.2–160.4	24.5	Heptane	$C_{29}H_{44}O_2$	82.03	81.85	10.44	10.61		
8	Benzaldehyde	1	1/2	199.3–199.8	43.3	Heptane	$C_{29}H_{36}O_2$	83.62	83.54	8.71	8.55		
9	*p*-Hydroxybenzaldehyde	3	1/2	262.4–263.1	35.2	Acetic acid	$C_{29}H_{36}O_3$	80.53	80.33	8.39	8.10		
10	Salicylaldehyde	1	1/2	216.7–217.0	18.9	Toluene	$C_{29}H_{36}O_3$	80.53	80.37	8.39	8.59		
11	2,4-Dichlorobenzaldehyde	1	4	209.9–210.4	59.6	Heptane	$C_{29}H_{34}Cl_2O_2$	71.73	71.91	7.06	6.96	14.61	14.65
12	5-Chlorosalicylaldehyde	1	6	214.2–215.9	29.2	Benzene	$C_{29}H_{35}ClO_3$	74.58	74.86	7.55	7.49	7.59	7.58
13	*o*-Chlorobenzaldehyde	1	1/2	226.3–226.9	23.5	Toluene	$C_{29}H_{35}ClO_2$	77.22	77.20	7.82	7.76	7.86	8.02
14	Veratraldehyde	1	1/2	231.2–231.9	52.5	Heptane	$C_{31}H_{40}O_4$	78.12	78.17	8.46	8.60		
15	Pyruvic aldehyde	2	1/4	196.2–197.1	34.8	Benzene	$C_{25}H_{34}O_3$	78.50	78.38	8.96	8.78		
16	Chloral	2	6	218.8–219.3	65.6	Toluene	$C_{24}H_{31}Cl_3O_2$	62.94	63.28	6.82	7.01	23.23	23.05
17	2-Methyl-2-pentenal	1	18	190.1–190.5	18.5	Heptane	$C_{28}H_{40}O_2$	82.30	82.15	9.87	9.52		
18	2-Ethyl-2-hexenal	1	3	210.2–210.6	38.4	Heptane	$C_{30}H_{44}O_2$	82.46	82.46	10.16	9.89		
19	2-Thiophenaldehyde	1	1/4	223.3–223.7	42.0	Heptane	$C_{27}H_{34}O_2S$	76.75	76.68	8.11	8.41	[c]	

[a] The compounds in Table 1 were all prepared following Procedure A. [b] 1, Heptane; 2, benzene; 3, glacial acetic acid; 4, water. [c] Sulfur, %: calcd. 7.57; found 7.64.

Experimental[9]

The compounds described in this paper have been prepared by two procedures—modifications of the original Baeyer synthesis. In both cases, the choice of precipitant was determined by spot testing during the initial reaction period. One ml. of the reaction mix was added to 3 ml. of each of the four selected precipitants and when crystal formation was noted, the reaction mixture was quenched with the chosen precipitant as indicated in the tables.

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(9) All melting points are corrected.