

TABLE II
 ^1H N.M.R. SPECTRA OF COMPOUNDS CONTAINING THE $\text{HCF}_2\text{CF}_2(\text{CF}_2)_x\text{CF}_2\text{CF}_2\text{CH}_2\text{O}$ GROUP

Compound	δ , p.p.m.	$J_{\omega\text{F}}$, c.p.s.	$\omega - 1$	$\alpha + 1$	α
			$J_{(\alpha+1)\text{F}}$, c.p.s.	$J_{(\omega-1)\text{F}}$, c.p.s.	$J_{(\alpha+2)\text{F}}$, c.p.s.
$\text{HCF}_2\text{CF}_2\text{CH}_2\text{OH}$	αH	3.98			
	ωH	5.94	54	13.0 ($\alpha + 1$)F	1.5 (ω) = ($\alpha + 2$)
	OH	4.46		4.5 ($\omega - 1$)F	
$\text{H}(\text{CF}_2)_4\text{CH}_2\text{OH}$	αH	4.12		15.5	...
	ωH	6.08	51.5	5.0	
	OH	4.72			
$\text{H}(\text{CF}_2)_6\text{CH}_2\text{OH}$	αH	4.12		15.0	...
	ωH	6.05	55.5	5.0	
	OH	4.65			
$[\text{HCF}_2\text{CF}_2\text{CH}_2\text{O}]_3\text{B}$	αH	4.25		13.0	... ^a
	ωH	5.87	54.0	4.0	
$[\text{H}(\text{CF}_2)_4\text{CH}_2\text{O}]_3\text{B}$	αH	4.39		13.0	...
	ωH	6.00	52.0	5.0	
$[\text{H}(\text{CF}_2)_6\text{CH}_2\text{O}]_3\text{B}$	αH	4.43		13.0	...
	ωH	5.98	51.5	5.0	

^a The αH to ($\alpha + 2$)F coupling is barely visible in this compound. Line broadening prevents its observation in the other compounds.

Company. Boron trichloride was obtained from the Matheson Company.

(b) **Typical Preparation: 2,2,3,3-Tetrafluoropropyl Borate.**—A Fisher and Porter Flowrator No. 08F-1/16-4/35 tube with glass ball float was calibrated by measuring the weight increase of pyridine used to absorb boron trichloride at various meter readings over timed intervals. In a 5-l. three-necked flask equipped with a stirrer, a reflux condenser protected with a Drierite drying tube, and a gas dispersion tube was put 3.71 kg. (28.1 moles) of 2,2,3,3-tetrafluoropropanol. The calculated amount of boron trichloride necessary to form the borate was metered into the alcohol over 9 hr. The flow rate varied during addition so that completeness of reaction was followed toward the end of the addition by infrared detection of the alcoholic OH band. The mixture was heated at approximately 60° for 2 hr. with a slow dry nitrogen sweep to remove dissolved hydrogen chloride and then distilled through a 65-cm. heated column packed with Raschig rings. Recovered was 814 g. of unreacted alcohol and 2.61 kg. (88.4%) of the borate ester, b.p. 202–206°.

Anal. Calcd. for $\text{C}_3\text{H}_9\text{BF}_2\text{O}_3$: B, 3.01. Found: B, 2.80. The analysis is obtained by titration of the boric acid from ester hydrolysis in the presence of mannitol. Other elemental analyses (C, H, F) were not satisfactory but structures are confirmed from the identity of the starting alcohols and the proton n.m.r. spectra of the products, *i.e.*, the OH peak due to alcohol disappears while the fluoroalkyl group spectrum remains. B^{11} n.m.r. chemical shifts are those expected for borate esters.^{5,6,9} The proton spectra and coupling values are shown in Table II. No peaks due to species other than $\text{H}(\text{CF}_2\text{CF}_2)_x\text{CH}_2$ are seen.

(c) **Instrumentation.**— B^{11} n.m.r. spectra were obtained utilizing a Varian V-4300 high resolution n.m.r. spectrometer operating at 12.83 Mc. ^1H n.m.r. spectra were obtained utilizing a Varian A-60 high resolution n.m.r. spectrometer.

(d) **Reactions of Borates with Amines.**—Stoichiometric quantities of borate ester and amine were placed in n.m.r. sample tubes, and chemical shifts of the resultant solutions were measured utilizing boron trichloride and boron triethyl as standards.⁵ Shifts, where reaction occurred, were at $\delta = -2$ to 0 p.p.m. compared to $\delta = -16$ to -18 p.p.m. for the borate.⁶

Acknowledgment.—The authors thank Professor Thomas P. Onak of the Los Angeles State College for stimulating discussions during this work.

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Explosive Formation of Manganates under Very High Pressures

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Received November 15, 1963

In the course of a study of the behavior of solid oxidizing agents under very high pressures, the oxidation of MnO_2 by either KClO_3 or KNO_3 in the presence of alkali has been investigated. The oxidation of MnO_2 to K_2MnO_4 by KClO_3 or KNO_3 in the presence of KOH at atmospheric pressure is a well-known, solid-state method for preparation of the manganate. This study of the oxidation under very high pressures (10–50 kbars) has shown that the reaction becomes explosive at a comparatively low temperature (80–90°) above about 19 kbars.

Experimental

The high-pressure unit used in this work (Tem-Pres Research, Inc., Model SJ-100) was a uniaxial press with simple Bridgman anvils.¹ The reagents were thoroughly mixed in a mortar and the power was placed inside a nickel ring (0.75 in. o.d., 0.5 in. i.d., 0.018 in. thick) and sandwiched between two platinum covers 0.001 in. thick. Since the ratio between the internal diameter of the ring and its thickness was about 28, the pressure on the sample was essentially uniform along the ring diameter.² The sample and the anvils were heated by means of an external furnace. The temperature was measured by means of a chromel–alumel thermocouple placed in direct contact with the sample. The samples were brought to the desired pressure at room temperature and subsequently heated at constant pressure.

(1) F. Dacheille and R. Roy in "Modern Very High Pressure Techniques," R. H. Wentorf, Ed., Butterworths, London, 1962, p. 163.

(2) M. Myers, F. Dacheille, and R. Roy, ASME Preprint No. 62-WA-255 (1962).

(9) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

The temperatures of explosion at the various pressures (large circles, Fig. 1) were determined by recording the temperature at which a detonation was clearly heard during the heating of the sample at constant pressures. As a consequence of the explosion the containing rings were broken and the material was splashed against the protective steel shields which surround the anvils. Analysis of the material collected on the shields always showed the presence of manganate, of residual MnO_2 , and, in the case of the MnO_2 - KClO_3 - KOH system, of chloride ions.

Results

The results obtained are illustrated in Fig. 1. The small circles give the temperatures at which the formation of the manganate first became detectable at the various pressures. At atmospheric pressure the oxidation of MnO_2 was appreciable at about 170° in the presence of either KClO_3 , KNO_3 , or air. Pressures between 10 and 19 kbars apparently had a retarding action on the reaction, particularly in the MnO_2 - KNO_3 - KOH system. Above about 19 kbars the reaction proceeded explosively.

Samples with MnO_2 : KClO_3 molar ratios of either 1 or 0.5 exploded at temperatures which were the same within the experimental errors. An explosion temperature of 135° has been determined for the MnO_2 - KClO_3 - KOH system at 100 kbars, in agreement with the value extrapolated linearly from the 19-50-kbar region. No reaction could be detected in the explosive pressure region up to $\sim 10^\circ$ below the explosion temperature. Substitution of NaOH for KOH in the MnO_2 - KClO_3 system did not affect the temperature of explosion within experimental error. A 1:1 molar mixture of MnO_2 and KClO_3 heated to 335° at 41 kbars in the absence of alkali did not explode and only a very slight decomposition of KClO_3 could be detected (Cl^- test). No decomposition of KClO_3 was observed after heating the mixture to 210° at 41 kbars. No explosion and no decomposition were observed in a MnO_2 - KClO_3 mixture heated at 170° in the presence of water.

Discussion

The catalytic decomposition of KClO_3 at atmospheric pressure in the presence of MnO_2 as a catalyst proceeds at a high velocity at temperatures between 290 and 300° for various MnO_2 - KClO_3 mixtures, including those used in these experiments.³ The presence of water has been reported to enhance the catalytic decomposition rate.⁴

It is, therefore, apparent that high pressures exert a remarkable retarding action on the catalytic decomposition of the chlorate. This result is consistent with earlier data⁴ which showed the negative influence of pressures up to about 500 bars on the decomposition of KClO_3 in the presence of MnO_2 . KClO_3 was only slightly decomposed (Cl^- test) when heated alone up to 450° under a pressure of 41 kbars. The 1:2 molar mixture of MnO_2 and KNO_3 did not explode in the

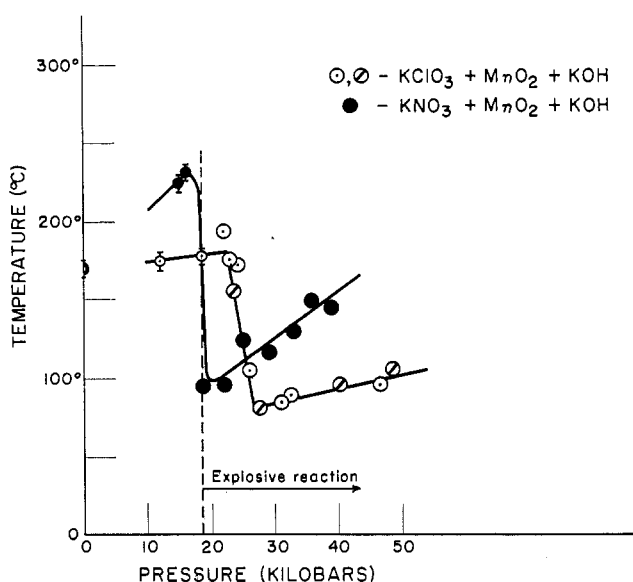


Fig. 1.—Temperatures of explosion (MnO_2 : $\text{KClO}_3 = 1$, \circ ; MnO_2 : $\text{KClO}_3 = 0.5$, \odot ; MnO_2 : $\text{KNO}_3 = 0.5$, \bullet) and temperatures of incipient reaction (MnO_2 - KClO_3 , \square ; MnO_2 - KNO_3 , \blacklozenge) as a function of pressure.

absence of KOH and no decomposition of the nitrate (NO_2^- test) was observed when this mixture was heated to 210° at 24 kbars.

Thus, the explosive reaction was only observed when alkali was present, the pressure was greater than 19 kbars, and the temperature above 80 - 90° . This observation implies that, at least, the thermal initiation of these explosions, which occur at comparatively low temperatures, should be attributed to a very rapid formation of the manganate at pressures above 19 kbars. The sharp transition from a normal to an explosive reaction, at about 19 kbars for both the MnO_2 - KClO_3 - KOH and the MnO_2 - KNO_3 - KOH systems, suggests the existence of a phase transition in MnO_2 at this pressure or the formation of a complex K-Mn-O-H species which catalyzes the reaction. The high pressure phase thus formed would be characterized by a much higher reactivity toward KClO_3 and KNO_3 than the low pressure phase. It should be mentioned in this connection that samples subjected to pressures in excess of 20 kbars and subsequently heated at pressures below 20 kbars do not explode, suggesting that the high-pressure phase cannot be preserved at the lower pressures. Neither the phase diagram of pure MnO_2 nor the interaction of MnO_2 with alkali hydroxides has been investigated at high pressures.

It is apparent from the figure that the temperatures of incipient reaction and the explosion temperatures are both increased when the pressure is increased. A negative influence of the pressure on the rate of reaction was also observed for the reaction $\text{BaO}_2 + \text{MnO}_2 = \text{BaMnO}_4$. At atmospheric pressure the temperature of incipient reaction is about 350° and the reaction is already much faster at 370° . Under 30 kbars no reaction was detected up to 410° and no explosive reaction was observed up to 410° . An increase of the

(3) J. A. Burrows and F. E. Brown, *J. Am. Chem. Soc.*, **48**, 1790 (1926); see also J. D. Woods and F. E. Brown, *Proc. Iowa Acad. Sci.*, **62**, 258 (1955).

(4) H. M. McLaughlin and F. E. Brown, *J. Am. Chem. Soc.*, **50**, 782 (1928).

explosion temperature with increasing pressure, up to the very high pressure range, has been reported for a number of solid explosives.⁵

The fact that for the systems under investigation the rates of both the normal and of the explosive reactions are decreased by a pressure increase could be interpreted on the assumption that, whatever the activated complex may be, the activation volume⁶ is positive for both the normal and the explosive reactions.

Acknowledgments.—The authors are pleased to acknowledge the support of this research by the Advanced Research Projects Agency and the Army Research Office (Durham). E. M. was supported by the National Research Council of Italy.

(5) F. B. Bowden and A. D. Yoffe in "Fast Reactions in Solids," Academic Press, New York, N. Y., 1958, p. 38.

(6) D. Lazarus and N. H. Nachtrieb in "Solids under Pressure," W. Paul and D. M. Warshauer, Ed., McGraw-Hill Book Co., New York, N. Y., 1963, p. 43; R. W. Keyes, *ibid.*, p. 71.

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The Infrared Spectrum of Sodium α -Oxyhyponitrite¹

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Received November 26, 1963

The α -oxyhyponitrite ion has been assigned the structure $\left[\begin{array}{c} \text{O} \\ \diagup \\ \text{O} > \text{N}-\text{N}-\text{O} \end{array} \right]^{2-}$ on the basis of recent calorimetric measurements.² Addison, *et al.*,³ had previously come to the same conclusions by comparing the ultraviolet spectra of NO_3^- , NO_2^- , and $\text{N}_2\text{O}_2^{2-}$ with that of $\text{N}_2\text{O}_3^{2-}$. While investigating some reactions of nitric oxide, the author had occasion to prepare this compound and measure its infrared spectrum. The details of this infrared spectrum and a partial Raman spectrum presented here are also consistent with the above structure.

Experimental

The white compound, $\text{Na}_2\text{N}_2\text{O}_3$, was prepared according to the procedure described by Addison.

*Anal.*⁴ Calcd.: N, 22.91; Na, 37.65; O, 39.34. Found: N, 22.36; Na, 35.40; O, 40.00.

The infrared spectra were obtained as Nujol and hexachlorobutadiene mulls using a Beckman IR-4 spectrophotometer with NaCl and CsBr optics. The Raman spectrum was obtained using a Cary Model 81 recording Raman spectrophotometer.

Results and Discussion

A typical infrared spectrum of $\text{Na}_2\text{N}_2\text{O}_3$ is shown in Fig. 1. Samples from several different preparations

(1) This work was sponsored by The International Nickel Company, Inc.

(2) H. R. Hunt, J. R. Cox, and J. D. Ray, *Inorg. Chem.*, **1**, 938 (1962).

(3) C. C. Addison, G. A. Gamien, and R. Thompson, *J. Chem. Soc.*, 338 (1952).

(4) The analyses were carried out by Huffman Microanalytical Laboratories, Wheatridge, Colo.

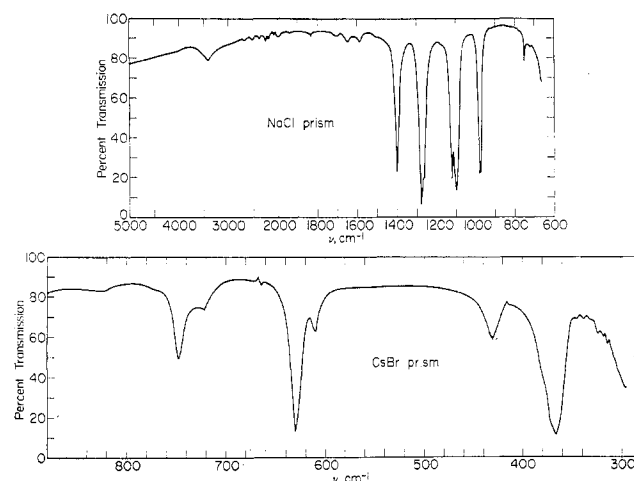


Figure 1.

were identical except for the occasional appearance of impurity bands due to NaHCO_3 and water. A partial Raman spectrum was obtained from a saturated aqueous solution of $\text{Na}_2\text{N}_2\text{O}_3$ at room temperature. Unfortunately, the solution decomposed too rapidly to obtain reliable Raman spectra. When it decomposed, the compound liberated oxides of nitrogen which were evolved as tiny bubbles of gas. These appear as "noise" on the recorded Raman spectrum. For the very intense Raman bands the "noise" presents few difficulties, but it is a serious problem for the weak Raman bands. The results of the partial Raman spectrum are presented in Table I, along with the observed

TABLE I

THE RAMAN AND INFRARED FREQUENCIES (cm^{-1}) OF $\text{N}_2\text{O}_3^{2-}$

Raman	Infrared	Assignment
1380 s ^a	1400 s ^a	Antisymmetric NO_2 stretch
1240 w	1280 s	Symmetric NO_2 stretch
1110 m	1120 s {	N-N stretch
	1100 s }	
975 s	980 s {	N-O stretch
	970 s }	
745 w	747 w	NO_2 bending
	630 m } [?]	N-NO bending
605 m	610 w }	
425 w	430 w	N-NO bending
	367 m	ON- NO_2 out-of-plane bending
		ON- NO_2 out-of-plane bending

^a s, strong; m, medium; w, weak.

infrared frequencies. The facts that the bands at 1100 and 980 cm^{-1} are only single bands in solution and that at least nine other strong bands are observed in the infrared spectrum of the solid indicate that the two bands at 1100 and the two at 980 cm^{-1} represent a total of only two fundamentals.

There are two types of configurations which will be considered for the $\text{N}_2\text{O}_3^{2-}$ ion. One is $\text{O}-\text{N}-\text{NO}_2^{2-}$ and the other is $\text{O}-\text{N}-\text{O}-\text{N}-\text{O}^{2-}$. Both of these arrangements have at least two possible types of symmetry, C_s and C_{2v} . These configurations cannot be distinguished from one another by the number of infrared-active fundamentals or by the number of frequencies coincident in the infrared and Raman spectra.