KURZE MITTEILUNGEN

Bis am 20. des Monats bei der Redaktion eingehende kurze Mitteilungen werden in der Regel am 15. des folgenden Monats veröffentlicht
Es werden auch Manuskripte aus dem Auslande angenommen

Concerning a Purported Polymorph of Li_2O_2 *

In a physicochemical study of lithium peroxide, Rode, Dobrynina and Golder[1] reported a phase transition in Li_2O_2 at 225 °C. As part of our work concerning the use of lithium peroxide as an atmosphere regenerant, i.e., absorption of CO_2 and concommitant release of O_2, it was felt desirable to investigate this reported phase transition. Specifically, it was planned to utilize such a transition to improve the physical properties and chemical activity of Li_2O_2.

A cursory examination of Li_2O_2 in our laboratory by means of differential thermal analysis (DTA) failed to disclose any evidence of such a phase transition on Li_2O_2 samples prepared in our laboratory. A more comprehensive study was then undertaken.

The Russian authors do not indicate the method by which they synthesized Li_2O_2. In addition to our own methods of preparation[2] we used the well known methods of Pierron,[3] Winternitz[4] and Strater.[5] The different preparations all gave consistent X-ray diffraction patterns, corresponding to what Rode *et al.* call α-Li_2O_2. The thermal behavior of these samples was almost identical, the minor differences being attributed to the different level of impurities in these preparations.

The reported α-β transformation was exothermic and irreversible, hence the α form should be metastable in respect to the stable β form. The preparation of such a metastable form might well require very particular conditions. Also, the presence of impurities could be required to initiate the transition, to make rearrangements of strained structures possible or to form a solid solution. Several additives, all lithium compounds, were tried with this thought in mind.

We were unable to produce the beta form by any of these means, which included four different methods of preparation and the addition of three other compounds. A minute exothermic effect was occasionally observed in the 225 °C region, but X-ray diffraction did not reveal any structural change.

Thermogravimetric Analysis

A Chevenard thermo-balance was used. The heating rate was 5 °C per minute under an argon flow of 125 ml/minute. The weight loss started at 350 °C and reached completion at 420 °C. The observed weight loss was 98 % of the active oxygen value, obtained by titration. The sample itself analyzed at 97 % Li_2O_2. Rode *et al.* (loc. cit.) obtained with similar heating rates and in air slightly different results. Decomposition started at 290 °C and was complete at 350 °C, for a preparation reported to be 98.93 % Li_2O_2.

Differential Thermal Analyses

Consistent with the TGA data we observed a strong endotherm between 350 and 400 °C, which corresponds to the loss of active oxygen. DTA was performed by modifying the Chevenard furnace and temperature programmer. A nickel block containing sample wells and sheathed 1/C or C/A thermocouples 1/16″ in diameter replaced the usual crucible and weighing device. The curves were recorded on an X–Y recorder with a response sensitivity of either 9½ or 12½ ° per inch (typical curves are shown in Figure 1).

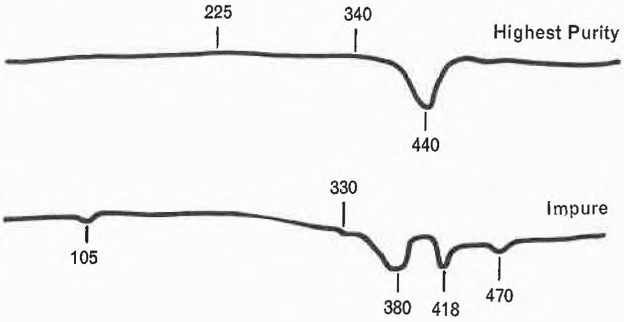

Fig. 1. DTA of Li_2O_2

On our highest purity material we could not observe any further thermal effects after the decomposition endotherm had returned to the base line. Slightly impure material however gave two small endotherms, one with its peak at 418 °C and the other at 470 °C. This preparation started to lose its oxygen much earlier and the peak of the decomposition endotherm was at 380 °C versus 440 °C with the pure material (these curves are shown in the figure).

The thermal behavior of the impure preparation is very similar to the thermograms of Rode *et al.* (loc. cit.), with the exception of the very strong exotherm starting at 210 °C with a peak at 321 °C. We never observed such an effect. In a few cases we had a very small exothermic effect at 225 °C, about 1/100 of the magnitude of the endo-

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* Submitted for publication April 11, 1963.

[1] T. V. Rode, T. A. Dobrynina and G. A. Golder, *Bull. Acad. Sci. URSS* (English Translation) *4* (1955) 545–53.

[2] *Chem. Eng. News, 1962* (Nov. 19) 56. Paper presented at the 14th Southeastern Regional Meeting of the A.C.S. at Gatlinburg (Tennessee) by W. W. Boardman jr. and R. O. Bach.

[3] P. Pierron, *Bull. Soc. Chim. France* (5) *6* (1939) 235.

[4] P. Winternitz, U.S. Pat. 2488485 (1949).

[5] H. H. Strater, U.S. Pat. 2962358 (1960).

thermic effect pertaining to the decomposition of Li_2O_2. We have no explanation for this small exothermic pip. Unlike the endotherms pertaining to the thermal decomposition of Li_2O_2, the ones at 418° and 470 °C are reversible. They show up as exotherms in the cooling cycle. We went thru 3 to 4 heating and cooling cycles repeatedly to prove this point.

Rode's interpretation of these effects were that the first one (415 °C in his case) corresponds to a polymorphic transition of LiOH, generated in the sample by exposure to moist air during the run. The second one (at 483°) was explained as the fusion of LiOH, which occurs at 471 °C. We believe these conclusions to be erroneous. In order to prove the origin of these effects, we added Li_2CO_3 and LiOH, separately or together, to pure lithium peroxide or oxide. The first endotherm is observed only in the presence of Li_2CO_3 at 402° to 418 °C. This then leads to the conclusion that a Li_2O–Li_2CO_3 eutectic is formed at this temperature. The second endotherm (at 445° to 470 °C) was identified as being due to the presence of LiOH. This can be attributed to a Li_2O–LiOH eutectic. Lithium fluoride was also added to Li_2O_2 during synthesis of the peroxide, to see if it might induce the beta transition. No effect was noted.

X-Ray Diffraction Analysis

Numerous preparations were investigated before and after heat treatments to above 225 °C. In all cases we observed the typical pattern of Li_2O_2 (Rode's α-Li_2O_2). Our d (Å) values coincide almost exactly with the values of Rode's α-Li_2O_2 and with earlier data by Feher[6].

We therefore conclude that we cannot confirm the existence of a beta phase in Li_2O_2 and we cannot find evidence of metastability in the lithium peroxide preparations we investigated. The high temperature endotherms in our samples were identified as a Li_2CO_3–Li_2O eutectic and a LiOH–Li_2O eutectic, respectively. It seems probable that the endotherms observed by the Russian authors at 415° and 483° are in fact also due to these same eutectics, even though they do not report the presence of carbonate in their samples. Reaction with atmospheric CO_2 could have caused the formation of Li_2CO_3 in their samples.

[6] F. Feher, I. Wilucki and G. Dost, *Chem. Ber. 86* (1953) 1429.

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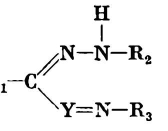
Darstellung substituierter vicinaler Triazole *

In unsere Untersuchungen über den Einfluß von Schwermetallionen, insbesondere denen des Kupfers, Nickels und Kobalts bei der Komplexbildung mit substituierten Glyoxalanil-arylhydrazonen vom Typ I[1]



(I)

R_1 = CH_3–CO–, C_2H_5COO–, –CN, Aryl–CO
R_2 = R_3 = Aryl, Hal/Alkyl-Aryl
Y = CH, C-Alkyl, C-Aryl

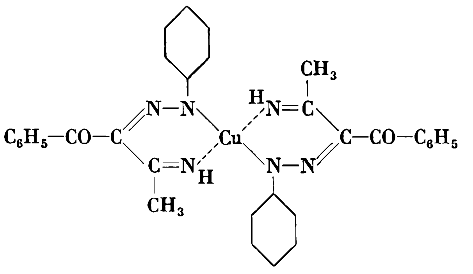
wurden auch Verbindungen vom Typ I, wo R_3 = H, also substituierte Glyoxal-imin-arylhydrazone, einbezogen.

Insbesondere sollte auch bei diesen Verbindungen der Einfluß des Kupfers untersucht werden, wie er bei den entsprechenden Formazylverbindungen vom Typ I, wo Y = N, R_2 = R_3, beobachtet wurde[2].

Wir wählten vorerst folgende Verbindung (über die Darstellung wird an anderer Stelle berichtet)

I R_1 = C_6H_5–CO–
R_2 = C_6H_5–
R_3 = H
Y = $(CH_3)C\equiv$

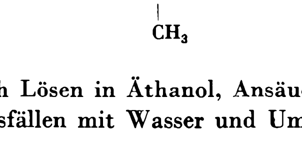
Wird diese Verbindung in Methanol bzw. Äthanol gelöst und mit einer ammoniakalischen Lösung eines Kupfer(II)-Salzes versetzt, dann bildet sich zuerst der entsprechende Kupferkomplex,



(II)

der sich auch als solcher isolieren läßt.

Wird dagegen die alkoholische Lösung erhitzt, dann nimmt die Reaktionslösung eine dunkelblaue Farbe an, der Komplex zerfällt, und beim Erkalten kristallisiert in Form weißer Nadeln das folgende Triazolderivat (III)



(III)

aus, das durch Lösen in Äthanol, Ansäuern mit wenig Salzsäure, Ausfällen mit Wasser und Umkristallisation

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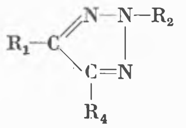
* Vorläufige Mitteilung. Eingegangen am 13. April 1963.

[1] B. Hirsch und A. Bassl, *Z. Chem. 2* (1962) 115, 276, 340; B. Hirsch und E. Förster, *Z. Chem. 2* (1962) 150 und *3* (1963) 29.

[2] B. Hirsch, *Liebigs Ann. Chem. 637* (1960) 189.

aus Äthanol von einer weiteren bei dieser Temperatur nur in geringen Anteilen gebildeten schwach gelben Substanz – darüber soll später berichtet werden – abgetrennt wird.

(III) erwies sich als identisch in seinen analytischen und spektroskopischen Daten mit dem von Wittig beschriebenen 2-Phenyl-4-methyl-5-benzoyl-triazol (1,2,3)[3]. Es wurde ferner gefunden, daß sich allgemein Verbindungen vom Typ I, wo Y= –C(Alkyl), –C-Aryl, R=H, in Äthanol mit ammoniakalischer Kupfersalzlösung umgesetzt – in den meisten Fällen schon nach kurzem Erhitzen – unter Zerfall der intermediär gebildeten Kupferkomplexverbindung mit guter Ausbeute in Triazole (IV)



(IV)

R_1, R_2 wie in I
R_4 = Alkyl, Aryl

überführen lassen.

Die Vorteile dieser Reaktion zeigen sich nicht nur in der leichten Variierbarkeit der Gruppierungen R_1, R_2 und R_4 in (IV), sondern auch in der einfachen Darstellungsweise von zum Teil bisher unseres Wissens noch nicht beschriebenen vicinalen Triazolen.

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[3] G. Wittig, F. Bangert und H. Kleiner, *Ber. dtsch. chem. Ges. 61* (1928) 1140.