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ON THE EXPLOSIVE PROPERTIES OF TETRAAZIDO-p-BENZOQUINONES

William H. Gilligan* and Mortimer J. Kamlet
Naval Surface Weapons Center, White Oak, Maryland 20910

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In 1969 E. Winkelmann[1] reported the preparation of 2,3,5,6-tetraazido-p-benzoquinone (I) which was prepared earlier by Ochwat and Fries[2] by a different route. Winkelmann reported that the compound was highly sensitive to shock and friction and decomposed explosively at 120°. These properties were of interest and prompted us to repeat the synthesis.

The method of Winkelmann in our hands proved to be erratic and better results were obtained using a phase transfer catalyst to effect the reaction between an aqueous solution of sodium azide and a methylene chloride solution of chloranil. The tetraazido compound (I) crystallized from carbon tetrachloride:methylene chloride solution in the form of chunky dark blue crystals which changed spontaneously on standing to a brownish powder with a green metallic sheen.

The results of impact tests on tetraazido-p-benzoquinone are presented below and compared with similar data for lead azide and lead styphnate, which are common initiating explosives.

Impact Sensitivity[a] of Lead Styphnate, Lead Azide and Tetraazido-p-Benzoquinone

Sample	50% Height (cm)	Std. Dev. (cm)
Lead Styphnate	8.8	0.16
Lead Azide	4.6	0.19
Tetraazido-p-Benzoquinone	<1.5[b]	--

a. Determined on a ERL-Type 12 impact machine; conditions were 2.5 kg weight, 05 flint paper, 35 mg sample weight per shot and 25 shots per sample.

b. The 1.5 cm height is the smallest that can be used on the ERL-12 impact machine.

The results indicate that the tetraazido compound is extremely sensitive to impact; so sensitive in fact that the true value could not be measured. The sensitivity of either crystal form was the same (<1.5 cm) insofar as it could be determined. In addition several samples exploded during gentle arrangement on the sandpaper used for the tests, which indicates that this material is extremely sensitive to friction. In short, tetraazido-p-benzoquinone is a far more dangerous substance to handle and manipulate in the dry state than either lead azide or lead styphnate, which are in themselves very dangerous materials.

While Winkelmann stated that (I) should only be prepared on a laboratory scale, we feel as chemists experienced in explosives, that the 24 g yield shown in his method is far too large to handle safely and is an invitation to a serious accident for an unwitting chemist; isolation of amounts larger than one or two hundred milligrams should be avoided under ordinary laboratory conditions. It should also be noted that for the preparation of 2,5-diazido-3,6-dichloro-p-benzoquinone (II) a 100% excess of sodium azide is recommended. This can and has at least in one instance[3] led instead to the tetraazidoquinone; a safer method for the preparation of (II) is to use phase transfer techniques with a stoichometric amount of sodium azide[4].

References

1. E. Winkelmann, Tetrahedron 25, 2427 (1969).
2. P. Ochwat and K. Fries, Ber. Dtsch. Chem. Ges. 56, 1299 (1923).
3. Private Communication from Prof. W. Moore, U of CA, Irvine, CA.
4. The diazido-dichloro-p-benzoquinone (II), while it does not explode upon heating, does have an impact sensitivity of 14 cm. This indicates that II is a sensitive explosive despite Winkelmann's contention that it has no explosive properties. It should be handled with due caution.