# RELATIVE STABILITIES OF THE ISOMERIC CYCLOHEXANE-1,2,3-TRIOL TRINITRATES AND 1,2-DIOL DINITRATES<sup>1</sup>

#### BY W. R. CHRISTIAN<sup>2</sup> AND C. B. PURVES

#### Abstract

Of the above trinitrates, the cis-cis-cis and the cis-trans-cis isomers melted at 70° and 88°C., respectively, but the racemic cis-cis-trans form remained as a colorless viscid oil. When dissolved in excess 0.105 N aqueous-alcoholic sodium hydroxide at 20°C., the *cis-cis-cis* isomer hydrolyzed most rapidly but formed least nitrite, and the solution developed most color. The same isomer evolved the smallest amount of oxides of nitrogen when kept at  $106^{\circ}$ C., but was more readily detonated by check then was the *cis cis cis* trinitrate. The relative readily detonated by shock than was the cis-trans-cis-trinitrate. The relative reactivities toward alkali and heat of the much more stable cis and trans-cyclohexane-1,2-diol dinitrates, which melted at 24° and 18.5°C., respectively, were as described for the trinitrates, but their relative sensitivities to shock were no less. All five compounds were new.

# Introduction

Although it is generally conceded that the explosive properties of an aliphatic nitrate increase with the number of nitrate groups, correlations between these properties and the details of chemical structure and reactivity are still highly incomplete. Much of the available information on chemical reactivity concerns the decomposition of various aliphatic nitrates in alkali, and the early work in this field was reviewed by Lowry, Browning, and Farmery (15). The cleavage of nitrate groups in alkali generally proceeded on both sides of the ester oxygen atom,  $\frac{1}{12}$  O  $\frac{1}{12}$  NO<sub>2</sub>, to yield either the parent alcohol and nitrate, or nitrite together with the corresponding aldehyde or ketone. Nitroglycerine, for example, gave nitrate and nitrite; Berl and Delpy (2) found a glycerol dinitrate among the products, but no mononitrate or glycerol. Conventional hydrolvsis to an alcohol dominated in acidic conditions, or when a reducing agent was present in the alkali. Lachman (12) confirmed these principles for nitrotartaric acid, and found that the amount of nitrite formed from nitromalic acid was independent of the temperature, of the concentration and excess of alkali, but varied with the solvent (13).

According to kinetic studies by Lucas and Hammett (16), the cleavages of t-butyl nitrate and of t-butyl chloride to the alcohol and isobutene in acid, neutral, and alkaline dioxane-water mixtures were so similar that the same mechanisms of solvolysis and elimination could be postulated. Although more benzyl alcohol was produced from benzyl nitrate than from benzyl chloride by solvolysis, the mechanisms were otherwise similar, with the exception that none was suggested for the redox cleavage producing benzaldehyde

Manuscript received June 7, 1951.

Contribution from the Division of Industrial and Cellulose Chemistry, McGill University and Pulp and Paper Research Institute of Canada, Montreal, Canada. <sup>2</sup> National Research Council of Canada Student, 1944-45. Present address: Colgate-Palmolive-Peet Company, Jersey City, N.J., U.S.A.

#### CHRISTIAN AND PURVES: DINITRATES

and nitrite from the benzyl nitrate. The hydrolysis of simple alkyl halides was also compared by Gand (8) with that of ethyl nitrate in neutral and slightly acidic systems containing potassium nitrate or silver iodide. Ethyl nitrate was observed to consume alkali more rapidly than its rate of hydrolysis would suggest. Other workers (9) found that the alkaline saponification of methyl-2,3,4-triacetyl-a-glucopyranoside-6-nitrate swiftly gave an almost quantitative yield of the methyl-3,6-anhydroglucoside, and that other mononitrates in the glucose series also yielded anhydro derivatives when the nitrate group could be eliminated by a mechanism of the Walden inversion type. When this mechanism was not available, as in methyl-2,3,4-trimethyl- $\beta$ glucoside-6-nitrate, saponification of the nitrate group was difficult, about 20% of nitrite was formed and the 2,3,4-trimethyl glucoside was recovered in about 75% yield. The other organic product was a resin presumably derived from trimethyl glucoside whose primary alcohol group had been oxidized to an aldehyde unit. Since these results were qualitatively the same as those obtained by saponifying halides and sulphonates in the sugar series, the analogy between aliphatic nitrates, halides, and sulphonates was strengthened. This analogy made it very probable that the mechanisms of elimination, solvolysis and substitution, described for halides and sulphonates in a series of articles by Winstein and his collaborators (24), would eventually find their counterparts for nitrate esters. The particular mechanism favored in a given reaction often depended upon the details of *cis-trans* isomerism and other spatial relationships.

The slow thermal decomposition of several simple aliphatic nitrates gave as principal initial products nitrogen dioxide and the aldehyde or ketone corresponding to the original nitrate (6), the final products from methyl nitrate containing nitric oxide and formaldehyde (1) or carbon dioxide, water, and nitrogen after explosive decomposition (25). Nitroglycerine yielded nitrogen dioxide as an initial product (22), and later work confirmed the fact that first order kinetics were obeyed (1, 21, 23); control experiments with added nitrogen dioxide, nitric acid, or moisture showed that the reaction was catalyzed by its products (23). The initial thermal decomposition of aliphatic nitrates thus appeared to resemble one of the mechanisms of saponification in being a redox reaction leading to carbonyl compounds and the elements of nitrous acid, including nitrogen dioxide.

As a result of calculations based on dipole moments, de Kreuk (5) concluded that liquid nitroglycerine existed as various *cis-trans* conformations originating in free rotation about the carbon-carbon bonds and in proportions depending on the solvent. A consideration of the forces of repulsion existing between the nitrate groups suggested that the *cis-cis-cis* would be less stable than the *cis-trans-cis* conformation by an energy factor equivalent to 6330 cal. per mole. The all-*cis* conformation was then tentatively assigned to nitroglycerine in the "labile" crystal habit melting at 2°C., because Hibbert and Fuller (11) had shown that the spontaneous change of this form to the "stable" type of melting point 12.8°C. caused the evolution of practically the same amount of heat, 6356 cal. The "stable" crystals were more sensitive to detonation by shock than the lower melting form, but results for liquid nitroglycerine were conflicting (7, 10, 11). This irregularity might possibly have been caused by the occlusion in the nitroglycerine of varying numbers of extremely minute gas bubbles (3). The "stable" allotrope had the greatest brisance (7), but the difference between the rates of detonation of the two crystal forms was small (7, 10). Explosion of 1 gm. of the "labile" crystals, on the other hand, produced more gaseous products, 560 cc., than the amounts, 518 cc. and 390 cc., obtained from the "stable" type and liquid nitroglycerine, respectively (7). If de Kreut's inferences were valid, *cis-trans* relationships between nitrate groups produced differences in explosive properties, either in a direct way, or indirectly through their effect on spatial relationships in crystal lattices.

Recent researches (4, 17) accumulated supplies of the three isomeric cyclohexane-1,2,3-triols and made it possible to assign the proper stereochemical configuration to each. The present article describes the behavior of the three corresponding trinitrates, and also of cis- and trans-cyclohexane-1,2-diol dinitrates, toward alkali, together with some observations on their explosive properties. These trinitrates (structures I, II, and III) were regarded as conformations of nitroglycerine that were rendered capable of independent existence because the presence of the cyclic structure abolished, or very greatly restricted, free rotation about the carbon-carbon bonds.



# Experimental

# cis-cis-cis-Cyclohexane-1,2,3-triol Trinitrate

A 5 gm. sample of the pure cis-cis-cis triol, melting correctly at 148°C., was added slowly, at 0°C. with stirring, to 20 parts by weight (67 cc.) of 98% nitric acid in which 15 gm. of phosphorus pentoxide had been dissolved. After one hour at 0°C. the mixture was stirred into 1 liter of ice and water, and several hours later the product was recovered, washed free of acid, and dried. Yield, 8.5 gm., or 84%; melting point 73° to 74°C. Recrystallizations from hot ligroin caused the material to separate as large thin plates belonging to the monoclinic, or possibly the triclinic, system, and melting at 74° to 74.5°C. Other organic liquids dissolved the substance freely at room temperature. Calc. for C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>O<sub>9</sub>: C, 27.0; H, 3.4; N, 15.7%. Found: C, 26.9, 27.1; H, 3.8, 4.0; N(Dumas), 15.6, 15.7%; N(micro-Kjeldahl), 15.6, 15.7%.

Similar crude yields resulted in this case when the phosphorus pentoxide was omitted from the nitration mixture; also when the latter was replaced with glacial acetic acid, 100 cc., acetic anhydride, 38 cc., and 98% nitric acid, 18 cc. Nitrations with this mixture lasted from 15 min. to 16 hr. without influencing the yield.

#### cis-cis-trans-Cyclohexane-1,2,3-triol Trinitrate

A similar nitration of 5 gm. of the pure *cis-cis-trans* triol, melting correctly at 123.5° to 124.5°C., yielded an oil which was made acid-free by repeated washing in distilled water near 0°C.; the oil being recovered on the centrifuge after each wash. A solution of the oil in ether was decolorized with absorbent carbon, was dried over anhydrous sodium sulphate, and was evaporated under reduced pressure. After being kept *in vacuo* over phosphorus pentoxide, 7.6 gm. (75%) of a clear, very faintly yellow oil remained with a refractive index of  $n_{D}^{21}$ , 1.4895. Calc. for C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>O<sub>9</sub>: N, 15.7%. Found: N, 15.6, 15.6%.

The substance showed no tendency to crystallize from solvents, nor after being kept for six months at  $-5^{\circ}$ C. It was a colorless glass at  $-40^{\circ}$ C.

### cis-trans-cis-Cyclohexane-1,2,3-triol Trinitrate

A similar nitration of the pure *cis-trans-cis* triol, melting correctly at 109° to 110°C., was for one hour at  $-5^{\circ}$ C. The crude product (66% yield and m.p. 83° to 84°C.) when recrystallized from hot ligroin yielded large rodlike prisms of either the monoclinic or triclinic systems and melting at 88° to 88.5°C. Calc. for C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>O<sub>9</sub>: N, 15.7%. Found: N, 15.8, 15.6%.

## cis-Cyclohexane-1,2,-diol Dinitrate

The pure *cis* diol, 10 gm. of m.p. 99°C., when nitrated at  $-5^{\circ}$ C. for 30 min. gave an oil which was washed and dried as described above for the *cis-cis-trans* triol trinitrate. The product, 14.7 gm. or 83%, melted at 23° to 25°C., but wasteful recrystallizations from hot ligroin were necessary to yield the pure substance as prismatic rods with melting point 24.5° to 25°C. and refractive index,  $n_D^{21}$ , 1.4790. Calc. for C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>O<sub>6</sub>: N, 13.6%. Found: N, 13.4, 13.4%.

## trans-Cyclohexane-1,2,-diol Dinitrate

The pure *trans* diol, m.p. 104°C., when nitrated as described for the *cis* isomer, gave an 80% yield of an oil which crystallized as small irregular plates,

m.p. 17° to 19°C. Recrystallization from hot ligroin reduced the yield of pure material to 56% melting at 18.5° to 19°C. Calc. for  $C_6H_{10}N_2O_6$ : N, 13.6%. Found: N, 13.5, 13.6%.

# Decomposition of the Nitroxycyclohexanes in Alkali

In all cases the solvent was 50% aqueous ethanol by weight, or 60 parts of 95% ethanol to 40 parts of water by volume, the mixtures used being free of acidic impurities and dissolved carbon dioxide.

The experiments with the trinitrates were carried out at  $20 \pm 0.05$ °C. in 100 cc. volumetric flasks containing 0.001 mole of each nitrate, and zero time was taken as the moment when the addition of 25 cc. of 0.4184 N aqueousalcoholic sodium hydroxide brought the original solution up to the mark. The solution was promptly and thoroughly mixed. After various times 10 cc. aliquots were made acid by adding 25 cc. of 0.045 N hydrochloric acid, and the excess was back-titrated with 0.01013 N sodium hydroxide to pH 8.0. A Coleman pH meter was used because of the marked color of certain of the solutions (Figs. 1 and 2).



FIG. 1. Rate of neutralization of 0.105 M sodium hydroxide by 0.01 M solutions of the 1,2-dinitroxycyclohexanes at 100°C., and of the cis-cis-cis-1,2,3-trinitroxy derivative at 0°C. Solvent, 50% aqueous ethanol.

Since the dinitrates reacted only very slowly at 20°C., they were examined at 100°C. The initial solution of 100 cc. was promptly divided into 10 cc. aliquots, each of which was contained in a 4 oz. bottle fitted with a screw top and a rubber gasket. The bottles were then heated in a steam oven for various times, were cooled, and the contents titrated as before. Blanks run without the nitrate showed that the glass of the bottles neutralized up to 3.7 cc. of the 0.01 N alkali as the time of heating was extended to five hours, but the corresponding plot, a reversed S in shape, was used to correct the results (Fig. 1).

CHRISTIAN AND PURVES: DINITRATES



FIG. 2. Rate of neutralization of 0.105 M sodium hydroxide by 0.01 M solutions of the 1,2,3-trinitroxycyclohexanes at 20°C. Solvent, 50% aqueous ethanol.

After the titration to pH 8, each aliquot was diluted to 100 cc. and examined for color and nitrite content. The latter was determined by adding 1 cc. of Miller's (20) dimethylaniline – hydrochloric acid reagent to 25 cc. of the solution and estimating the depth of color produced by the yellow nitroso derivative four hours later. A photoelectric colorimeter with a blue filter was used, and the details of the technique were as described elsewhere (9). The blanks consisted of other 25 cc. volumes of each original solution adjusted to approximately the same pH with 1 cc. of 5 N hydrochloric acid instead of with 1 cc. of Miller's reagent. Known, accurate dilutions of pure 0.028 M sodium nitrite were used to establish the calibration plot and a plot of log per cent transmission of light against the concentration of nitrite was linear within the range studied, as was expected (9). Figs. 3 and 4 summarize the results.









The remainder of each neutralized, diluted aliquot was then examined for its content of yellow color, the photoelectric calorimeter being used with a blue filter against distilled water as the standard. As the nature of the coloring material was unknown, it was necessary to assume that the amount was proportional to the intensity of color, and the plots in Fig. 5 were based on this assumption. No determinations were made with the cyclohexanediol dinitrates, both of which yielded solutions whose yellow-brown colors were much less intense than those from the trinitrates. As the intensity varied with the pH, a 10 cc. aliquot of the completely hydrolyzed *cis-cis-trans*trinitrate was diluted to 100 cc. and acidified, when it became nearly colorless. The pH was then varied from 2.2 to 9.4 by the cautious addition of increments of concentrated sodium hydroxide, the over-all volume change being less than





5%. A plot of the pH against the log per cent transmission of light formed a smooth curve slightly convex to the pH axis and showed that the action of pH was reversible within the limits cited.

# Sensitivity to Impact

These tests were made on the Rotter Impact Machine, in which a blow caused by a steel ball falling from a variable height was communicated to the sample resting on a steel anvil. The minimum height required to produce detonations in 50% of the runs was found by trial and was compared with the corresponding heights for nitroglycerine and for trinitrotoluene, which were standard substances. The results are in Table I.

FABLE I
---------

Substance	М.р., °С.	Drop test,** cm.	Ignition test		Bergerreen Turch
			Fumes, °C.	Ignition, °C.***	test,† mgm. NO/gm.
Dinitrates cis	24.5	A (300) B 60	170		0.27
trans	19	$ \begin{array}{cccc}                                  $	165	185	0.67
Trinitrates cis-cis-cis††	74.5	$egin{array}{ccc} A & 55 \ B & 60 \ C & 60 \end{array}$	$\begin{array}{c} 155\\ 170 \end{array}$	$180\\182$	0.95
<i>cis-cis-trans</i> ††† (an oil)		$ \begin{array}{cccc} A & 40 \\ B & 34 \\ C & 38 \end{array} $	$\begin{array}{c} 155\\ 163\end{array}$	172	3.5
cis-trans-cis	88.5	A 85 B 85	155	• • • •	8.6

EXPLOSIVE PROPERTIES OF THE DI-AND TRINITROXYCYCLOHEXANES\*

\* Samples used in Tests A were retested four months later (Series B). Samples prepared four years later by Mr. N. S. Whittall were used for Tests C. \*\* Height of fall of steel ball required to produce detonation. Nitroglycerine, 8 cm.; tri-

nitrotoluene, 100 cm.

\*\*\* Definite but mild explosions.
† After 20 hr. at 106°C. and atmospheric pressure. From data in Fig. 6.
†† A 6-gm. sample gave 1.23 times the power of trinitrololuene in the ballistic mortar test.
††† A 6-gm. sample 1.28 times as powerful as T.N.T. in the ballistic mortar test.

#### Thermal Stability

The Bergmann-Junk-Mayrhofer (18, 19) method was used, the 0.1 gm. samples being heated at  $106 \pm 1^{\circ}$ C. for various times and the liberated oxides of nitrogen absorbed in 10 cc. of 5% potassium iodide. The equivalents of iodine liberated per mole of sample were estimated with 0.01 N sodium thiosulphate and were plotted against the time of heating (Fig. 6). Table I contains the results after heating for 20 hr., expressed as mgm. nitric oxide per gram sample.



FIG. 6. Rates of evolution of oxides of nitrogen, expressed as equivalents of iodine per mole, from the 1,2,3-trinitroxy and 1,2-dinitroxycyclohexanes when kept at 106°C.

### **Results and Discussion**

None of the five nitrates liberated an appreciable amount of acid when kept at room temperature in water, but all could be decomposed at convenient rates when dissolved in an excess of 0.105 N sodium hydroxide in 50% aqueous ethanol. The reactions were followed by noting the rate of disappearance of alkali, the rate of formation of nitrite, and the rate at which a yellow color developed in the solutions.

It is obvious from Fig. 1 that the cis-dinitrate (circles) neutralized more than the theoretical 2 moles of alkali, and reacted more rapidly than the trans-isomer (triangles); also that the rate for the cis-cis-trinitrate at 0°C. (crosses) was comparable to that of the cis-dinitrate at 100°C. Multiplication of adjacent nitrate groups therefore greatly increased the over-all reactivity toward alkali. Results for the trinitrates at 20°C. (Fig. 2) showed that the cis-cis-cis isomer rapidly consumed nearly 2 moles of alkali and that the rate then diminished rather abruptly. Since the plot at 0°C. (Fig. 1) had no similar break, it appeared likely that the saponification proceeded by two reactions whose activation energies were different. The plot at 0°C. for the cis-cis-trinitrate and that for the cis-cis-trans isomer at 20°C. happened to be almost superposable at all times up to five hours. By analogy with the results in Fig. 1, it was expected that the *cis-trans-cis*-trinitrate would be least reactive toward alkali, but this position was taken by the *cis-cis-trans* isomer (squares). The initial point on the cis-cis-trans plots in Figs. 2, 3, and 5 appeared displaced in the direction of a greater consumption of alkali, although the reaction of the original trinitrate toward water was neutral. An unknown, readily saponified impurity or a small amount of an *aci*-modification of the kind encountered by Gand (8) in ethyl nitrate, might have been present in this uncrystallized trinitrate, but the proper explanation was not determined.

The unexpected position of the *cis-trans-cis*-trinitrate in Fig. 2 was perhaps related to the superior amount of nitrite which this isomer produced (Fig. 3), and in this case the *cis-cis-trans*-trinitrate occupied the intermediate position.

Although these plots at 20°C. appeared to be linear, the mechanics of nitrite formation were probably complex because the data for the *cis-cis-cis* isomer at 0°C. clearly indicated a more extensive initial reaction (Fig. 4, crosses). The same type of plot was given by the *cis*-dinitrate at 100°C, and possibly by the *trans* isomer, which definitely produced more nitrite per mole of sodium hydroxide consumed. Since the plot for the *trans*-dinitrate at 100°C, was accurately superposable on that for the *cis-trans-cis*-trinitrate at 20°C, the mechanism of nitrite formation was probably independent of temperature and identical for both of these *trans* compounds.

It was noted that the color assumed by the alkaline solutions of the nitrates ranged in intensity from slight vellow-brown for the dinitrates at 100°C. to a clear, very deep yellow for the *cis-cis-cis*-trinitrate at 20°C. Fig. 5 shows that the intensity of color imparted by this trinitrate, even at 0°C., exceeded those given by the other two isomers at 20°C., and that the cis-cis-trans-trinitrate was once more in the intermediate position. These intensity measurements were all made at pH 8 because the depth of color decreased in a reversible fashion with pH. The assumption that the intensity of color was proportional to the amount of the color-producing substances led to the conclusion that the cis-trans-cis-trinitrate, which produced most nitrite and presumably the greatest amount of alkali-sensitive carbonyl compounds, nevertheless gave the smallest yield of colored products. The production of about 0.9 mole of nitrite from the three nitrate groups in the *cis-trans-cis* isomer might, however, have resulted in a 90% yield of a monoketone such as (IV), which would remain nearly colorless in alkaline solution. On the other hand, the 0.5 mole of nitrite released by the cis-cis-trinitrate might correspond to the formation of 25% of a diketone of type (V), which would probably behave as an indicator yielding a colored charged particle (VI) in the higher pH range (14). A further breakdown of a diketone would also explain the high consumption of alkali by the cis-cis-trinitrate (Fig. 2). These speculations are at present entirely unsupported by experimental evidence.



Submission of the five nitrates to a temperature of 106°C., as in the standard Bergmann-Junk test for the thermal stability of explosives, liberated oxides of nitrogen that were estimated as equivalents of iodine per mole of sample (Fig. 6). The *cis-trans-cis*-trinitrate proved to be the least stable, and was also distinguished by the failure of the plot to pass near the origin of the co-ordinates. The amounts of the oxides liberated thermally were in the same sense as the production of nitrite in the saponifications, both for the trinitrates

and for the much more stable trans and cis dinitrate. Table I, Column 5. expresses the decompositions after 20 hr. in the customary way as mgm. nitrous oxide per gm. sample. The ignition test (Table I) revealed little difference between the nitrates, but sensitivity to detonation by shock was definitely greater for the cis-cis-trinitrate and cis-dinitrate than for the corresponding *trans* compounds. These results paralleled the rate and amount of alkali consumed by the nitrates (Figs. 1 and 2) and not the amount of nitrite formed during saponification. The *cis-cis-trans*-trinitrate, however, consumed less alkali than its isomers but was much more sensitive to shock. Although this trinitrate was an uncrystallized raceme, the unexpectedly high sensitivity could hardly be attributed to impurities or to the occlusion of gas, because a sample prepared four years later by another worker gave a concordant result. The explanation of this anomaly remained obscure. Since both the *cis* and *trans* dinitrates were molten when tested for sensitivity, the results must be attributed to their difference in molecular shape rather than to difference in crystal habit. The same inference might possibly be drawn for the all-cis and all-trans trinitrates, because their respective sensitivities duplicated those of the cis and trans dinitrates within the observational error.

As already mentioned, crystalline nitroglycerine of the "stable" type was more sensitive to detonation by shock than the "labile" isomer. Analogy with the present work suggests that the respective conformations would be *cis-cis*cis and cis-trans-cis, but de Kreuk's arguments reversed this assignment. The superior over-all reactivity of the cis-cis-cyclohexanetriol trinitrate toward alkali was unexpected in the light of the general chemical behavior of halide, acetyl, or sulphonyl substituents (24), and the mechanisms underlying sensitivity and thermal stability obviously depended in different ways on *cis-trans* configurations. It was unfortunate that the comparative inaccessibility of the *cis-cis-trans*, and the great inaccessibility of the *cis-trans-cis*, cyclohexane-1,2,3-triols prevented a closer study of these problems.

## Acknowledgments

The work was extensively financed by the National Research Council and one of us (W.R.C.) wishes to thank the Council for a Studentship. The authors record their great indebtedness to Mr. M. C. Fletcher, Department of Mines and Resources, for providing the data on sensitivity, ignition and power recorded in Table I; to Prof. R. P. D. Graham for the observations on crystal habit; and to Dr. C. J. Gogek for supplementing the stocks of the cyclohexane triols.

#### References

 APPIN, A., TODES, O., AND KHARITON, YU. J. Phys. Chem. (U.S.S.R.), 8:866. 1936. Chem. Abstracts, 31: 2437. 1937. 1910.

BERL, E. AND DELPY, M. Ber. 43: 1421.  $\mathbf{2}$ 

3. BOWDEN, F. P., MULCAHY, M. F. R., VINES, R. G., AND YOFFE, A. Proc. Roy. Soc. (London), A, 188:311. 1947. 4. CHRISTIAN, W. R., GOGEK, C. J., AND PURVES, C. B. Can. J. Chem. 29: 911. 1951.

DE KREUK, L. J. Rec. trav. chim. 61: 819. 1942.
 DENIGÈS, G. Compt. rend. 202: 1998. 1936.
 DSERSHKOVICH, A. A. AND ANDREEV, K. K. Z. ges. Schiess- u. Sprengstoffw. 25: 353, 400. 1930. Chem. Abstracts, 25: 1674. 1931.
 GAND, E. Bull. soc. chim. 11: 511. 1944. Chem. Abstracts, 40: 2062. 1946.
 GLADDING, EDWARD K. AND PURVES, C. B. J. Am. Chem. Soc. 66: 76. 1944.
 HACKEL, J. Roczniki Chem. 16: 213. 1936. Chem. Abstracts, 30: 8619. 1936.
 HIBERT, H. AND FULLER, G. P. J. Am. Chem. Soc. 35: 978. 1913.
 LACHMAN, A. J. Am. Chem. Soc. 43: 577. 1921.
 LACHMAN, A. J. Am. Chem. Soc. 43: 2084. 1921.
 LEWIS, G. N. AND CALVIN, M. Chem. Revs. 25: 308. 1939.
 LOWRY, T. M., BROWNING, K. C., AND FARMERY, J. W. J. Chem. Soc. 117: 552. 1920.
 LUCAS, G. R. AND HAMMETT, L. P. J. Am. Chem. Soc. 64: 1928. 1942.
 MCRAE, J. A., GOGEK, C. J., AND MOIR, R. Y. To be published.
 MAYRHOFER, F. M. Z. ges. Schiess- u. Sprengstoffw. 13: 425. 1918. Chem. Abstracts, 13: 3320. 1919.
 MEERSCHEIDT-HÜLLSEN, J. V. Z. ges. Schiess- u. Sprengstoffw. 35: 107. 1940. Chem.

13: 3320. 1919.
19. MEERSCHEIDT-HÜLLSEN, J. V. Z. ges. Schiess- u. Sprengstoffw. 35: 107. 1940. Chem. Abstracts, 34: 7605. 1940.
20. MILLER, E. H. Analyst, 37: 345. 1912.
21. ROBERTSON, A. J. B J. Soc. Chem. Ind. (London), 67: 221. 1948.
22. ROBERTSON, R. J. Chem. Soc. 1241. 1909.
23. ROGINSKI, S. Physik. Z. Sowjetunion, 1: 640. 1932.
24. WINSTEIN, S. AND GRUNWALD, E. J. Am. Chem. Soc. 70: 828. 1948.
25. ZEL'DOVICH, YA.B. AND SHAULOV, YU.KH. J. Phys. Chem. (U.S.S.R.), 20: 1359. 1946. Chem. Abstracts, 41: 2969. 1947.