[Contribution from the Department of Chemistry, University of Kentucky]

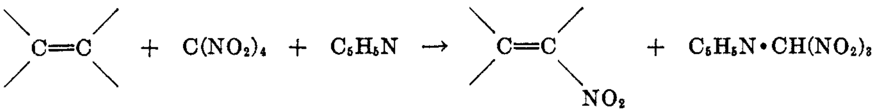
THE STRUCTURE OF TETRANITROMETHANE

JOHN M. PATTERSON

Received May 2, 1955

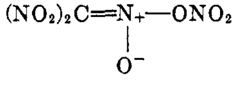
The possible applications of tetranitromethane as a rocket propellant and as a diesel fuel additive (1) have aroused renewed interest in the compound. The chemistry was thoroughly investigated several years ago although some uncertainty remained as to the true structure of the compound.

Most of the reactions concern the behavior of tetranitromethane toward alkali or toward acid or alkaline solutions of reducing agents. For example, in the presence of strong alkali, potassium *aci*-nitroform and potassium nitrate (2) are formed, while the corresponding ammonium salts can be isolated from the reaction with liquid ammonia (3). Alkaline hydrazine produces the salt of *aci*-nitroform, nitrite ion, and nitrogen (4). Other reducing agents which react similarly in alkaline media are sodium sulfite, sodium arsenite (5), potassium ferrocyanide (6), phenylhydrazine, and thiourea (7). In acid media, titanous chloride reduces tetranitromethane to guanidine and nitrous acid (8). More interesting is the ability of tetranitromethane to behave as a nitrating agent toward certain olefins or aromatic hydrocarbons (9) or as a nitrosating agent toward tertiary amines (10).



$$C_6H_5N(CH_3)_2 + C(NO_2)_4 + C_5H_5N \rightarrow C_6H_5N(NO)CH_3 + CH_2O + C_5H_5N \cdot CH(NO_2)_3$$

The problem of structural assignment to tetranitromethane arises from the observation that one of the four nitro groups in the compound is highly reactive. Early workers interpreted this to mean that one of the nitro groups differs from the others. Thus, Willstätter (11) postulated the nitrone type structure I, while the behavior of tetranitromethane as a nitrating agent led Schmidt (9) to advance a nitro nitrite structure II.



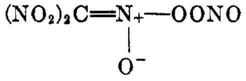
$$(NO_2)_2C{=}\overset{+}{N}(O^-){-}ONO_2$$

I

$$(NO_2)_3CONO$$

II

To account for the oxidizing properties of the substance, Krauz and Stepanek (12) suggested the peroxide structure III. Robinson (13), however, favors the symmetrical structure IV because, if the strong inductive effects of the nitro groups are considered, the oxidative capacity can be explained. Furthermore, it was pointed out that a difference in reactivity of nitro groups in tetranitromethane is not what is observed, but rather a difference in the reactivity of two molecules—tetranitromethane and the *aci*-nitro configuration of nitroform.



$(NO_2)_2C{=}\overset{+}{N}(O^-){-}OONO$

III

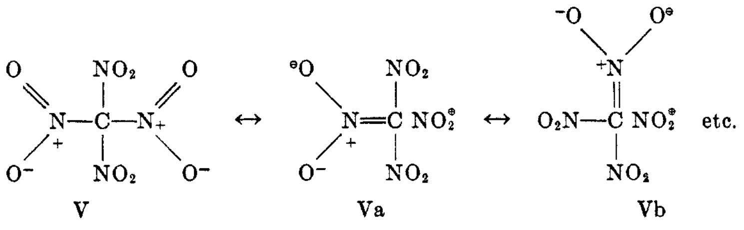
$C(NO_2)_4$

IV

Other structures have been postulated to explain the observed color reaction of tetranitromethane with olefins (14) or with Lewis bases (15). Macbeth and Harper (16) believed that the color arose from the isomerization of a nitro group to a nitrite group because of the similarity of the spectrum of the colored complex with that of the alkyl nitrites. Macbeth and Graham (17) pointed out that the spectrum obtained on standing in an alcohol solvent was the same as that observed by Hantzsch and Voight (18) for the salt of *aci*-nitroform. This ultraviolet absorption band, which formed on standing after a few minutes with Lewis bases and after several days with the olefins, is merely a spectral observation of tetranitromethane behaving as a nitrating agent. The color complex has also been said to be a polarization aggregate maintained by electrostatic forces (19).

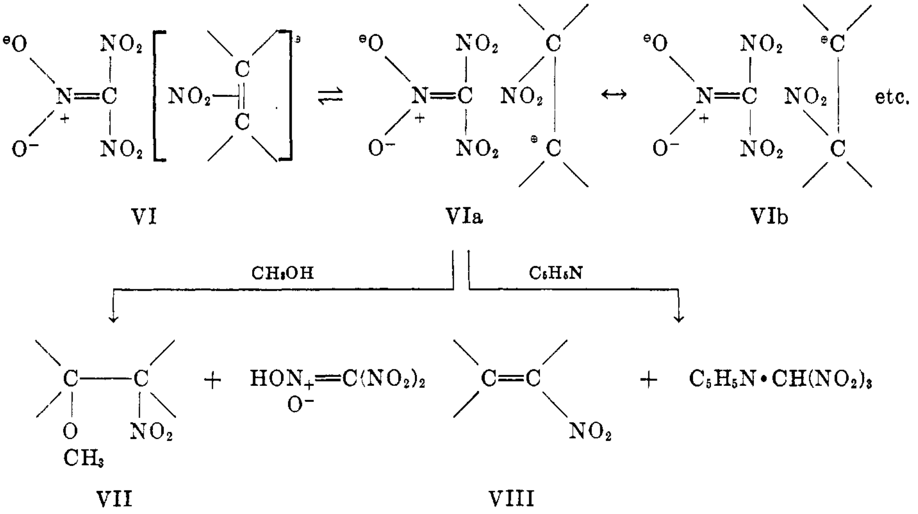
Although many of the physiochemical measurements have been interpreted to favor both the symmetrical and unsymmetrical structures, conclusive evidence for the symmetrical configuration is obtained from electron diffraction studies (20) and infrared spectral measurements (21) of the vapor. The dipole moment of tetranitromethane should be zero if the symmetrical structure is correct. Even though these measurements differ appreciably from zero (some are the same order of magnitude as that expected of the nitro nitrite structure II), they are usually cited in support of the symmetrical structure (22). These data may be unreliable because of the use of impure samples of tetranitromethane (21).

The purpose of this paper is to present a structure for tetranitromethane in terms of modern electronic theory which will explain the observed chemical behavior as well as the formation of colored complexes resulting from interaction with labile nucleophilic centers. Structurally tetranitromethane is best represented by a resonance hybrid whose contributing ionic forms are of the same type observed in the hyperconjugation of olefins (23).



V Va Vb

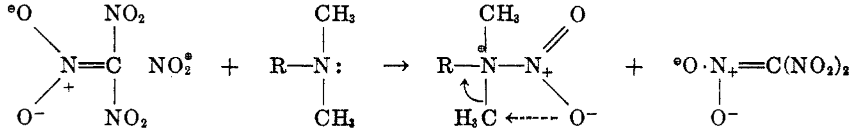
The contribution of the ionic forms to the ground state will be small since their formation requires a separation of charges. That they do contribute some is evidenced by the light yellow color observed in thick layers of tetranitromethane (21). Curiously enough, Macbeth and Henderson (8) arrived at the conclusion that NO_2^+ is easily removed from tetranitromethane by application of the theory of alternate polarities. In the presence of electron donors, such as olefins, the contribution of the ionic forms (Va–Vb) to the resonance hybrid is probably greater than in the ground state and these ionic structures may interact with π-electrons to form a π-complex VI, which may or may not be colored. This π-complex may isomerize further to colored structures VIa–VIb which result from the interaction of the nitronium ion with sp^3 hybrid orbitals. That these structures, VIa–VIb, exist is evidenced by the decomposition products VII–VIII. The intensity of the color of the complex should increase as electrons become more available. Thus, tetramethylethylene gives a more intense coloration than does ethylene (14) and N-methylpiperidine gives a deeper color than tetrahydrothiapyran which in turn gives a deeper color than tetrahydropyran (15). Likewise, since the colored complexes involve a separation of charges, the color of the complex should be more intense in polar solvents. This is verified by the observation that the color intensity increases as the polarity of the solvent is increased (15).



Under suitable conditions, the complex will decompose. In the presence of alcohol, β-alkoxynitro compounds (VII) are formed, while in the presence of pyridine, nitroölefins (VIII) are produced (9). Similar color complexes are observed with Lewis bases (24).

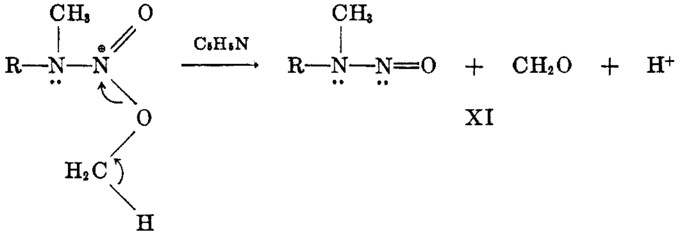
In the presence of a base, tetranitromethane V–Vb reacts to produce the salt of the *aci*-nitroform and nitrate ion, which arises from the reaction of the nitronium ion with base. Similarly, the oxidation reactions result from the reaction of nitronium ion, or of nitrate ion, with reducing agents.

The conversion of tertiary amines to N-nitroso amines results from the reaction of the ionic structures Va–Vb to form structure IX.



Va IX

The nitrammonium ion IX undergoes nitrolysis of a carbon-nitrogen bond in a manner similar to that observed in the action of nitric acid on tertiary amines (25), accompanied by a simultaneous 1,3-shift of the incipient carbonium ion to the oxygen of the nitro group to form X.



X XI

The compound X undergoes decomposition, not unlike that observed in the decomposition of nitronic esters (26), into the N-nitrosamine XI and formaldehyde. The group which forms the most stable carbonium ion in the tertiary amine will be the one displaced if this mechanism is correct. This is found to be the case. Thus, the reaction of ethyldibenzylamine (27) with tetranitromethane produces 14% of the N-nitrosodibenzylamine and 70% of the N-nitrosoethylbenzylamine.

A similar structural representation for bromotrinitromethane explains the ability of this compound to behave as a brominating agent (28).

SUMMARY

The chemical properties of tetranitromethane have been examined and reinterpreted in terms of modern electronic theory. The structure assigned herein adequately explains the observed chemical behavior and the formation of colored complexes resulting from interaction with olefins and Lewis bases.

Lexington, Kentucky

REFERENCES

(1) Hager, *Ind. Eng. Chem.*, **41**, 2168 (1949).
(2) Schmidt, *Ber.*, **52**, 400 (1919).
(3) Franklin and Kraus, *J. Am. Chem. Soc.*, **27**, 191 (1905).
(4) Macbeth and Pratt, *J. Chem. Soc.*, **119**, 1356 (1921).
(5) Baillie, Macbeth, and Maxwell, *J. Chem. Soc.*, **117**, 880 (1920).
(6) Chattaway and Harrison, *J. Chem. Soc.*, **109**, 171 (1916).
(7) Macbeth and Orr, *J. Chem. Soc.*, 534 (1932).

(8) Henderson and Macbeth, *J. Chem. Soc.*, **121**, 892 (1922).
(9) Schmidt and Fischer, *Ber.*, **53**, 1529 (1920); Schmidt, Schumacher, Böjen, and Wagner, *Ber.*, **55**, 1751 (1922).
(10) Schmidt and Fischer, *Ber.*, **53**, 1537 (1920); Schmidt and Schumacher, *Ber.*, **54**, 1414 (1921).
(11) Willstätter and Hottenroth, *Ber.*, **37**, 1775 (1904).
(12) Krauz and Stepanek, *Chem. Obzor.*, **11**, 153, 177 (1936).
(13) Robinson, *Nature*, **133**, 975 (1936).
(14) Slobodin, *J. Gen. Chem.*, (*U.S.S.R.*), **16**, 1698 (1946).
(15) Macbeth, *J. Chem. Soc.*, **107**, 1824 (1915).
(16) Harper and Macbeth, *J. Chem. Soc.*, **107**, 87 (1915).
(17) Graham and Macbeth, *J. Chem. Soc.*, **119**, 1362 (1921).
(18) Hantzsch and Voigt, *Ber.*, **45**, 85 (1912).
(19) Hammick and Young, *J. Chem. Soc.*, 1463 (1936).
(20) Stosick, *J. Am. Chem. Soc.*, **61**, 1127 (1939).
(21) Nicholson, *J. Chem. Soc.*, 1553 (1949).
(22) Lewis and Smyth, *J. Am. Chem. Soc.*, **61**, 3067 (1939).
(23) Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 91.
(24) Clarke, Macbeth, and Stewart, *Proc. Chem. Soc.*, **29**, 161 (1913).
(25) Lamberton, *Quart. Revs.* (*London*), **5**, 75 (1951).
(26) Weisler and Helmkamp, *J. Am. Chem. Soc.*, **67**, 1167 (1945).
(27) Labriola, Dorronsoro, and Verruno, *Anales assoc. quím. argentina*, **37**, 79 (1949).
(28) Schmidt, Bartholome, and Lubke, *Ber.*, **55**, 2099 (1922); Schmidt and Bartholome, *Ber.*, **57**, 2039 (1924).