(18) Even shorter $H^+\cdots O$ distances were reported[19] for a complex of "crown" ether with $\sim NH_3$ hydrogens.

(19) I. Goldberg, *Acta Crystallogr., Sect. B*, **31,** 2592 (1975).

(20) M. Bourgoin, K. H. Wong, J. Y. Hui, and J. Smid, *J. Am. Chem. Soc.*, **97,** 3462 (1975).

(21) Values of r's corresponding to the effective cross-sections of the PA and PTS anions have been estimated as 2.7 Å and those of the protonated 18/6 and 15/5 as 4.5 and 3.9 Å, respectively.

(22) The spectral characteristics of free PA ions and their loose ion pairs (PA–DCC/A complex) are assumed to be identical. Accordingly: $I = \epsilon_2(d + b) + \epsilon_1 a$, where a, b, d, ϵ_1, and ϵ_2 denote the uncomplexed acid, the complex (unionized), the free ions, and their extinction coefficients respectively. Hence, $H_0 = a + b + d$, $I_{max} = \epsilon_2 H_0$ and $I_0 = \epsilon_1 H_0$. Let us denote the ratio $(d + b)/a[CR]$ as K_C'. Accordingly: $K_C' = (I - I_0)/(I_{max} - I)[CR]$, $K_C = b/a[CR]$, $K_D = d^2 f^2/b$. It follows that:

$$K_C' = K_C + K_C K_D \Lambda' \, 10^{-3}/f^2{}_K \qquad (7)$$

(23) M. K. Dalley, D. E. Smith, R. M. Izatt, and J. J. Christensen, *J. Chem. Soc., Chem. Commun.*, 90 (1972).

(24) D. E. Fenton, M. Mercer, and M. R. Truter, *Biochem. Biophys. Res. Commun.*, **48,** 10 (1972).

(25) J. Smid, *Angew. Chem., Int. Ed. Engl.*, **11,** 112 (1972).

(26) N. Nae and J. Jagur-Grodzinski, *J. Chem. Soc.*, submitted for publication.

Decarboxylations of Azodicarboxylates by Nitrosonium and Nitronium Salts. Decarboxylative Oxidation and Substitution Reactions[1a]

Michael P. Doyle,*[1b] JoAnn L. Whitefleet,[1c] Donald J. DeBruyn,[1c] and Wendell Wierenga[1c]

Contribution from the Department of Chemistry, Hope College, Holland, Michigan 49423.

Received July 20, 1976

Abstract: Azodicarboxylates react with nitrosonium salts by two identifiable decarboxylative pathways, one leading to carbon dioxide, nitric oxide, and nitrogen (decarboxylative oxidation) and the other producing carbon dioxide and nitrous oxide (decarboxylative substitution). Association of the nitrosyl cation with the carbonyl oxygen of azodicarboxylate esters is observed in reactions with nitrosonium salts. Subsequent decomposition of the nitrosated ester is dependent on the stability of the alkyl cation generated in the decarboxylation process. The formation of nitrous oxide from nitrosation of potassium azodicarboxylate intimates the involvement of a linear dimer of nitrous oxide. Nitronium salts react with azodicarboxylates to yield dinitrogen tetroxide, nitrogen, and carbon dioxide. In contrast to nitrosative decomposition of azodicarboxylate esters, however, nitrative decomposition is not observably influenced by carbocation stability; these results permit a direct comparison of the electrophilic reactivity of nitrosonium and nitronium salts. The reactivity of azodicarboxylates toward dinitrogen tetroxide and of oxalates with nitrosonium and nitronium salts is also examined.

The decomposition of potassium azodicarboxylate by Bronsted acids[2] has been of considerable interest and synthetic importance due to the formation of diimide as a reactive chemical intermediate.[3] Surprisingly, analogous reactions of potassium azodicarboxylate or its derivatives with Lewis acids other than the proton have not been reported. If Lewis acids are generally capable of effecting decarboxylative substitution their reactions with azodicarboxylates will afford a new and valuable route to azo (dinitrogen) compounds. Reactions of azodicarboxylates with nitrosonium salts are particularly interesting since decarboxylative substitution will result in the formation of **1,** a linear dimer of nitrous oxide.[4] Decomposition of **1** can occur by two pathways, one leading to $2N_2O$ and one yielding $N_2 + 2NO$. Similar reactions with nitronium salts are expected to result in the formation of dinitrodiazene (**2**), which is predicted to decompose to nitrogen and dinitrogen tetroxide. However, since nitronium and nitrosonium salts are powerful oxidants as well as strong Lewis acids, electron transfer reactions of azodicarboxylates with these ions must also be considered.

$$2A^+ + {}^-O_2C{-}N{=}N{-}CO_2{}^- \rightarrow A{-}N{=}N{-}A + 2CO_2 \qquad (1)$$

$$\underset{\textbf{1}}{O{=}N{-}N{=}N{-}N{=}O} \qquad \underset{\textbf{2}}{O_2N{-}N{=}N{-}NO_2}$$

Results and Discussion

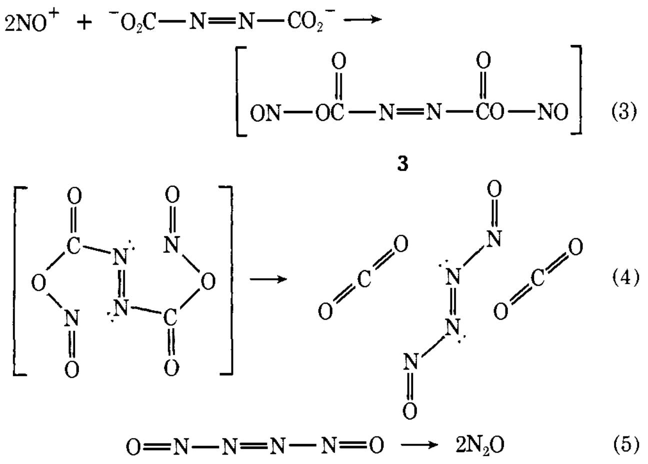
Reactions of Azodicarboxylates with Nitrosonium Salts. Azodicarboxylate compounds react rapidly with nitrosonium salts by divergent reaction pathways that reflect the structural nature of the azodicarboxylate derivative. Slow addition of potassium azodicarboxylate to 2 molar equiv of $NO^+BF_4^-$ in acetonitrile at room temperature under strictly anhydrous conditions[5] produces an immediate and rapid evolution of nearly equal amounts of nitrous oxide and carbon dioxide.

$$2NO^+ + {}^-O_2C{-}N{=}N{-}CO_2{}^- \rightarrow 2CO_2 + 2N_2O \qquad (2)$$

Nitric oxide and nitrogen are formed in a molar ratio of 2:1 as minor products in this reaction (<15% of the total nitrogen containing gaseous products). When allowances are made on the relative yield of carbon dioxide for the formation of $2NO + N_2 + 2CO_2$, the molar ratio of carbon dioxide to nitrous oxide is 1.0. The stoichiometry of the reaction of nitrosonium tetrafluoroborate with potassium azodicarboxylate, together with the observation of both nitrous oxide and carbon dioxide, suggests the operation of the substitutive decarboxylation pathway for the production of nitrous oxide (Scheme I). A similar scheme may explain the formation of diimide in the protonic decarboxylation of potassium azodicarboxylate.[6]

In Scheme I nitrosation of the azodicarboxylate dianion is described as occurring at oxygen. Subsequent decarboxylative

Scheme I



$$2\mathrm{NO^+} + {}^-\mathrm{O_2C{-}N{=}N{-}CO_2^-} \longrightarrow \left[\mathrm{ON{-}O}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}N{=}N{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}NO}\right] \tag{3}$$

3

$$\mathrm{O{=}N{-}N{=}N{-}N{=}O} \longrightarrow 2\mathrm{N_2O} \tag{5}$$

nitrosyl transfer from oxygen to nitrogen (eq 4), which may occur in a stepwise or concerted fashion, is a required step only if the site of initial nitrosation is oxygen rather than a diazene nitrogen.[7] However, attempts to identify **3** or a surrogate intermediate from reaction 2 in acetonitrile or carbon tetrachloride at low temperatures (−25 to −10 °C), by using IR spectral methods that were previously employed for the identification of nitryl azide,[4] were unsuccessful. Nevertheless the existence of an *O*-nitrosyl intermediate in the nitrosative decomposition of azodicarboxylate esters could be detected and the site of initial nitrosation could be determined.

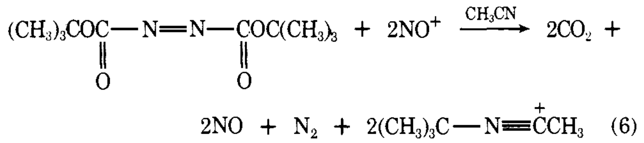
Di-*tert*-butyl azodicarboxylate reacts vigorously with 2 molar equiv of $\mathrm{NO^+BF_4^-}$ in acetonitrile at room temperature to produce nearly 5 molar equiv of gaseous products and the *N*-*tert*-butylacetonitrilonium ion. The gaseous products are nitric oxide, carbon dioxide, nitrogen, and nitrous oxide. Two equivalents of nitrosonium salt is required for complete decomposition of di-*tert*-butyl azodicarboxylate. When only 1 equiv of the nitrosonium salt is used, only one-half of the expected gas evolution is obtained and unreacted di-*tert*-butyl azodicarboxylate is recovered in an amount defined by a stoichiometric requirement of $2\mathrm{NO^+BF_4^-}$ + 1 azodicarboxylate.

The gaseous products were identified by IR, mass spectral, and GLC methods, and their yields were determined by GLC analyses. The ratio of the yield of carbon dioxide to the combined yields of nitrogen, nitrous oxide, and nitric oxide was constant (1.4). The yields of the nitrogen-containing products relative to carbon dioxide were observed to be 0.47 ($\mathrm{N_2}$), 0.95 (NO), and 0.025 ($\mathrm{N_2O}$).

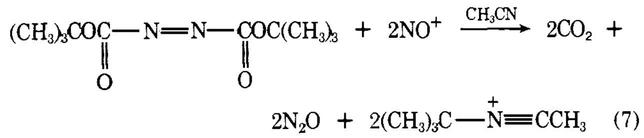
The *N*-*tert*-butylacetonitrilonium ion was observed by ^{1}H NMR spectroscopy[10] prior to quenching the reaction solution with water; the yield of this nitrilonium ion was greater than 80% (based on $2(\mathrm{CH_3})_3\mathrm{CN^+{\equiv}CCH_3}$ per azodicarboxylate) when the nitrosation reaction was carried out at room temperature. Only a trace of isobutylene was detectable.[11] After quenching with water, *N*-*tert*-butylacetamide was recovered in 48% yield.

The reaction of di-*tert*-butyl azodicarboxylate with nitrosonium salts provides a convenient source of the *tert*-butyl cation. When this reaction is performed in nitrile solvents, acetonitrile or benzonitrile, the corresponding *N*-*tert*-butylnitrilonium salts are formed; quenching with water yields *N*-*tert*-butylamides. In benzene, however, *tert*-butylbenzene and *p*-di-*tert*-butylbenzene are formed in less than 10% combined yield (8:1 ratio), and polymeric materical accounts for the principal fate of the *tert*-butyl group from the reaction of $\mathrm{NO^+BF_4^-}$ with di-*tert*-butyl azodicarboxylate.

The observation of the *N*-*tert*-butylacetonitrilonium ion and an integral molar ratio of nitric oxide to nitrogen of 2.0 suggests a reaction process (eq 6) in which the nitrosonium ion effects oxidative decomposition of the azodicarboxylate ester. The production of nitrous oxide, however, suggests an alternate reaction process, similar to that described in eq 2, in which decarboxylative nitrosyl transfer results in the formation of carbon dioxide, the *N*-*tert*-butylacetonitrilonium ion, and nitrous oxide (eq 7).[12]



$$(\mathrm{CH_3})_3\mathrm{CO}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}N{=}N{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OC(CH_3)_3} + 2\mathrm{NO^+} \xrightarrow{\mathrm{CH_3CN}} 2\mathrm{CO_2} + 2\mathrm{NO} + \mathrm{N_2} + 2(\mathrm{CH_3})_3\mathrm{C{-}\overset{+}{N}{\equiv}CCH_3} \tag{6}$$



$$(\mathrm{CH_3})_3\mathrm{CO}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}N{=}N{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{OC(CH_3)_3} + 2\mathrm{NO^+} \xrightarrow{\mathrm{CH_3CN}} 2\mathrm{CO_2} + 2\mathrm{N_2O} + 2(\mathrm{CH_3})_3\mathrm{C{-}\overset{+}{N}{\equiv}CCH_3} \tag{7}$$

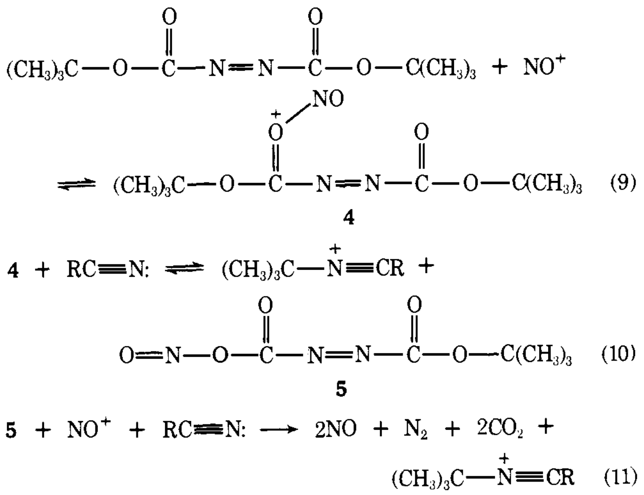
Comparison of eq 6 and 7 leads to the summary conclusion that the sole thermodynamic difference between the two reaction processes is the production of $2\mathrm{N_2O}$ or 2NO + $\mathrm{N_2}$ (eq 8). Formation of 2NO + $\mathrm{N_2}$ is thermodynamically favored.[13] Although the thermodynamically favored products are formed in reactions of di-*tert*-butyl azodicarboxylate with nitrosonium salts (98%), however, they do not constitute the major products from similar reactions with potassium azodicarboxylate (<15%).

$$2\,\mathrm{NO} + \mathrm{N_2} = 2\mathrm{N_2O} \tag{8}$$

Both diphenyl and diethyl azodicarboxylates are unreactive toward nitrosonium salts and can be recovered unchanged after treatment with $\mathrm{NO^+BF_4^-}$ under conditions identical with those employed with di-*tert*-butyl azodicarboxylate. However, infrared analyses of acetonitrile or nitromethane solutions of these dialkyl and diaryl azodicarboxylates and $\mathrm{NO^+BF_4^-}$ at −10 °C indicate that association of the nitrosonium ion with the carboxylate group does occur with each of these esters. A new intense carbonyl band is observed at 1860 cm^{-1} ($\mathrm{CH_3CN}$) or 1865 cm^{-1} ($\mathrm{CH_3NO_2}$), and an additional broad absorption, indicative of an O-substituted nitrosyl group, is found at 1640 cm^{-1}. The azodicarboxylate esters have an intense carbonyl absorption at 1770 ± 10 cm^{-1} ($\mathrm{CH_3CN}$) and no other absorption in the 1600-2800 cm^{-1} region. The absorptions at 1860 and 1640 cm^{-1} from the di-*tert*-butyl azodicarboxylate-$\mathrm{NO^+BF_4^-}$ system are observed to decrease with time (<15 min at 0 °C) as the gaseous products are evolved. No other absorptions in the 2500-1500 cm^{-1} spectral region, not associated with either reactants or products, could be detected.

These results suggest a mechanism for nitrosative decomposition of di-*tert*-butyl azodicarboxylate, outlined in Scheme II, in which nitrosation occurs at the carbonyl oxygen (**4**), as

Scheme II



$$(\mathrm{CH_3})_3\mathrm{C{-}O{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}N{=}N{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}C(CH_3)_3} + \mathrm{NO^+} \rightleftharpoons (\mathrm{CH_3})_3\mathrm{C{-}O{-}}\overset{\overset{\overset{+}{\mathrm{O}}\mathrm{{-}NO}}{\|}}{\mathrm{C}}\mathrm{{-}N{=}N{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}C(CH_3)_3} \tag{9}$$

4

$$\mathbf{4} + \mathrm{RC{\equiv}N{:}} \rightleftharpoons (\mathrm{CH_3})_3\mathrm{C{-}\overset{+}{N}{\equiv}CR} + \mathrm{O{=}N{-}O{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}N{=}N{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}C(CH_3)_3} \tag{10}$$

5

$$\mathbf{5} + \mathrm{NO^+} + \mathrm{RC{\equiv}N{:}} \longrightarrow 2\mathrm{NO} + \mathrm{N_2} + 2\mathrm{CO_2} + (\mathrm{CH_3})_3\mathrm{C{-}\overset{+}{N}{\equiv}CR} \tag{11}$$

is implied from the IR absorptions observed at 1860 and 1640 cm^{-1}.[14] Subsequent alkyl transfer yielding the mononitrite ester **5** and the *N*-*tert*-butylnitrilonium ion, followed by nitrosative decomposition of **5**, leads to the observed products. Although the stepwise mechanistic pathway for eq 10 and 11 cannot be definitively described with the present data, the integral role of carbocation stability in this process is suggested by the absence of a similar reaction with either diethyl or diphenyl azodicarboxylate and by the slow and incomplete reactions of di-*tert*-butyl azodicarboxylate with $NO^+BF_4^-$ in nonpolar solvents such as carbon tetrachloride or benzene. Scheme II, and in particular the stability of **4** toward direct decarboxylative decomposition, is consistent with the observation that when only 1 molar equiv of nitrosonium salt is used with di-*tert*-butyl azodicarboxylate, only one-half of the azodicarboxylate decomposes to products. Thus, oxidation of di-*tert*-butyl azodicarboxylate does not involve a two-electron transfer to NO^+ resulting in NO^-.[15] Instead, the azodicarboxylate ester reacts as a two-electron reducing agent to transform $2NO^+$ to 2NO.

Nitrosative decomposition of **5** may involve the expulsion of the second *tert*-butyl cation with the resulting formation of **3**. This process explains the production of nitrous oxide in reactions of $NO^+BF_4^-$ with di-*tert*-butyl azodicarboxylate and further supports the nitrosative substitution process that is described in Scheme I.

The uniqueness of azodicarboxylates in their reactions with nitrosonium salts was demonstrated by the comparative unreactivity of carboxylate esters toward $NO^+BF_4^-$ in acetonitrile at room temperature. Benzhydryl oxalate reacted slowly with $NO^+BF_4^-$ in acetonitrile primarily by an oxidative pathway,[16] leading to benzophenone and *N*-(diphenylmethyl)acetamide. After 1 h at room temperature less than one-third of the oxalate had reacted; after heating the reaction solution at 50 °C for 1 h and quenching with water, both benzophenone and *N*-(diphenylmethyl)acetamide were isolated (33 and 54% yields, respectively, based on total benzhydryl accountability). In contrast, sodium oxalate converts the nitrosonium ion into nitric oxide within 1 h at 25 °C. Carbon dioxide and nitric oxide are formed in equivalent amounts, which confirms the reaction stoichiometry of eq 12. No other products from reaction 12 are detected in yields >1% that of carbon dioxide. Benzyl phenylacetate was unreactive toward $NO^+BF_4^-$ in acetonitrile even after 20 h at 30 °C.

$$2NO^+ + {}^-OOC{-}COO^- \rightarrow 2NO + 2CO_2 \quad (12)$$

Reactions of Azodicarboxylates with Nitronium Salts. Nitronium salts, like nitrosonium salts, reacted rapidly with azodicarboxylates in acetonitrile at temperatures above 0 °C. Potassium azodicarboxylate yielded nitrogen (26% of total gaseous products), nitrous oxide (12%), and carbon dioxide (62%) as the sole gaseous products from reactions with 2 molar equiv of $NO_2^+BF_4^-$. Nearly 3 molar equiv of gaseous products (based on potassium azodicarboxylate) were formed in these reactions. After complete gas evolution, dinitrogen tetroxide was observed to be the only remaining product. The amount of N_2O_4 in acetonitrile was quantitatively determined by standard analytical methods, and when a 2:1 molar excess of $NO_2^+BF_4^-$ to potassium azodicarboxylate was used, the yield of N_2O_4 was, within experimental error, equal to one-half the molar amount of $NO_2^+BF_4^-$ that was consumed.

The formation of N_2, CO_2, and N_2O_4, together with their relative yields, suggests the stoichiometric relationship that is described in the following equation:

$$2NO_2^+ + {}^-O_2C{-}N{=}N{-}CO_2{}^{2-} \rightarrow N_2O_4 + 2CO_2 + N_2 \quad (13)$$

The production of nitrous oxide, which accounts for 32% of the reaction process leading to gaseous nitrogen products, is explained by eq 14: dinitrogen tetroxide reacts with potassium azodicarboxylate as nitrosonium nitrate[17] to give the same gaseous products as does nitrosonium tetrafluoroborate with potassium azodicarboxylate. The reaction described by eq 14 was confirmed independently by treating potassium azodicarboxylate with dinitrogen tetroxide in acetonitrile under the same reaction conditions as those used for reactions with $NO_2^+BF_4^-$.

$$2N_2O_4 + {}^-O_2C{-}N{=}N{-}CO_2^- \rightarrow 2N_2O + 2CO_2 + 2NO_3^- \quad (14)$$

Gas yields obtained from reactions in which the molar ratio of $NO_2^+BF_4^-$ to potassium azodicarboxylate is varied from 2 to 0.5 also suggest a competitive reaction. When the azodicarboxylate is treated with an equimolar amount of nitronium salt, the yield of gaseous products is 15% more than that expected from eq 13, and with a twofold molar excess of azodicarboxylate to $NO_2^+BF_4^-$ the gas yield is 29% greater than expected.

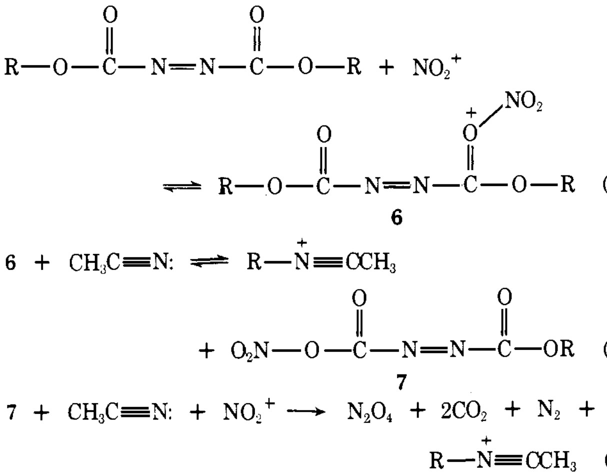
Nitronium tetrafluoroborate reacted rapidly with azodicarboxylate esters in acetonitrile at room temperature. The products from the reaction of 2 molar equiv of $NO_2^+BF_4^-$ with di-*tert*-butyl azodicarboxylate were nitrogen (30% of total gaseous products), nitrous oxide (4%), carbon dioxide (66%), dinitrogen tetroxide, and the *N*-*tert*-butylacetonitrilonium ion. Nearly 3 molar equiv of gaseous products were produced, and the molar ratio of CO_2 to $N_2 + 2N_2O$ was 2:1.1. Thus nitronium salts effect nitrative decarboxylation of di-*tert*-butyl azodicarboxylate with a reaction stoichiometry consistent with that of eq 13. However, as was observed in reactions of potassium azodicarboxylate with less than 2 equiv of nitronium tetrafluoroborate, the yield of gaseous products was greater than that predicted from a 2:1 $NO_2^+BF_4^-$ to di-*tert*-butyl azodicarboxylate stoichiometry. Indeed, reactions of this ester with an equimolar amount of $NO_2^+BF_4^-$ resulted in nearly 40% more gaseous products than expected and in the formation of both nitrous oxide ($N_2O{:}CO_2 = 0.10$) and nitric oxide ($NO{:}CO_2 = 0.12$). Similar results were observed when $NO_2^+BF_4^-$ was treated with a twofold molar excess of di-*tert*-butyl azodicarboxylate and point to competitive nitrosation of this ester by nitrosonium nitrate.

Both one- and two-electron oxidative pathways were considered for nitronium ion reactions with azodicarboxylates. In a two-electron oxidation, the nitronium ion would be converted to nitrite ion. Subsequent reaction of nitrite with the nitronium ion would yield the observed N_2O_4. If NO_2^+ undergoes reductive conversion to NO_2^-, reactions between the nitronium ion and azodicarboxylates would be expected to yield nitrite in amounts corresponding to the molar excess of gaseous products over the stoichiometry predicted from eq 13. However, the yield of nitrite, determined by sensitive analytical procedures specific for this ion, was less than 1% of the amount expected from reactions in which a limited amount of $NO_2^+BF_4^-$ was used to oxidatively decarboxylate the di-*tert*-butyl ester. Thus, in reactions with azodicarboxylates the nitronium ion can be reasonably described as a one-electron oxidant.[18]

Surprisingly, diethyl azodicarboxylate, which did not decompose upon treatment with nitrosonium salts, reacted vigorously with $NO_2^+BF_4^-$ to give the same gaseous products as did the di-*tert*-butyl ester, N_2O_4, and the *N*-ethylacetonitrilonium ion. The relative yields of CO_2, N_2, and N_2O were 64, 32, and 4%, respectively. A $2NO_2^+$:1 diethyl azodicarboxylate stoichiometry was observed even when the ester was used in twofold molar excess. No reaction between diethyl azodicarboxylate and N_2O_4 was observed.

The combined results from reactions of the nitronium ion with azodicarboxylate esters are reasonably explained by the

Scheme III



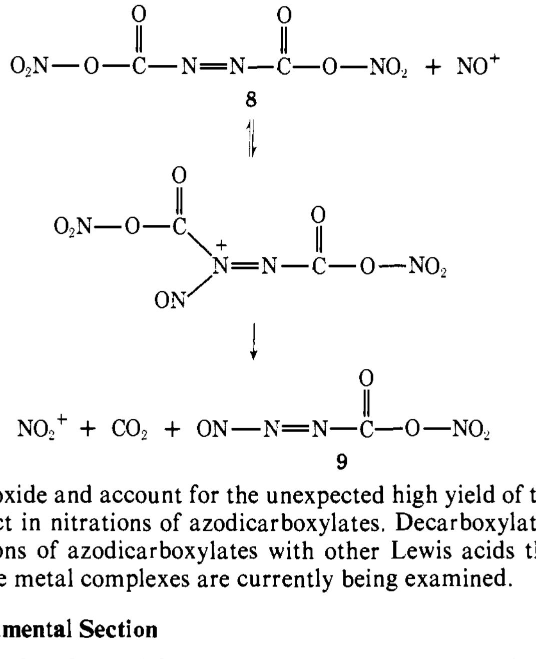
$$\mathrm{R{-}O{-}C({=}O){-}N{=}N{-}C({=}O){-}O{-}R} + \mathrm{NO_2^+} \rightleftharpoons \mathrm{R{-}O{-}C({=}O){-}N{=}N{-}C({=}\overset{+}{O}{-}NO_2){-}O{-}R}\ \ (\mathbf{6}) \quad (15)$$

$$\mathbf{6} + \mathrm{CH_3C{\equiv}N{:}} \rightleftharpoons \mathrm{R{-}\overset{+}{N}{\equiv}CCH_3} + \mathrm{O_2N{-}O{-}C({=}O){-}N{=}N{-}C({=}O){-}OR}\ \ (\mathbf{7}) \quad (16)$$

$$\mathbf{7} + \mathrm{CH_3C{\equiv}N{:}} + \mathrm{NO_2^+} \longrightarrow \mathrm{N_2O_4} + 2\mathrm{CO_2} + \mathrm{N_2} + \mathrm{R{-}\overset{+}{N}{\equiv}CCH_3} \quad (17)$$

mechanism in Scheme III. The nitronium ion, which is a stronger electrophile than the nitrosonium ion,[19] is able to effect displacement of even an ethyl cation from the carboxylate group of azodicarboxylate esters. Previous comparisons of nitrosonium and nitronium ion electrophilicities in electrophilic substitution reactions of aromatic compounds[20] and in hydride abstraction reactions[15c,21] have not been so direct as that observed in the present investigation of azodicarboxylates. Indeed, reactions of Lewis acids with azodicarboxylate esters may serve to directly measure their electrophilic reactivity.

Although it is not possible in the present study to definitively distinguish between the numerous possible decomposition pathways for **3** or its analogous nitrate ester, the formation of nitrous oxide in relatively high yield compared with nitric oxide in reactions of $NO_2^+BF_4^-$ with azodicarboxylates and the production of nitrous oxide even in nitrations of diethyl azodicarboxylate do point to an acid-catalyzed decomposition pathway for these unstable intermediates. For example, nitrosation of **8** by nitrosonium nitrate at a diazene nitrogen may effect decomposition of **8** to **9**, carbon dioxide, and the nitronium ion (eq 18); subsequent nitrosation of **9** would yield nitrous oxide and account for the unexpected high yield of this product in nitrations of azodicarboxylates. Decarboxylative reactions of azodicarboxylates with other Lewis acids that include metal complexes are currently being examined.



$$\mathrm{O_2N{-}O{-}C({=}O){-}N{=}N{-}C({=}O){-}O{-}NO_2}\ (\mathbf{8}) + \mathrm{NO^+} \rightleftharpoons \mathrm{O_2N{-}O{-}C({=}O){-}\overset{+}{N}(NO){=}N{-}C({=}O){-}O{-}NO_2} \longrightarrow \mathrm{NO_2^+} + \mathrm{CO_2} + \mathrm{ON{-}N{=}N{-}C({=}O){-}O{-}NO_2}\ (\mathbf{9}) \quad (18)$$

Experimental Section

Methods and Materials. Instrumentation has been previously described.[22] The Varian Model 485 digital integrator and the Varian CDS 101 data system were used to determine peak areas in GLC analyses. Low-temperature infrared spectral analyses were obtained on a Perkin-Elmer Model 621 grating spectrophotometer. Di-*tert*-butyl, diethyl, and diphenyl azodicarboxylates were commercially available and were used without further purification. Potassium azodicarboxylate was prepared from azodicarbonamide by hydrolysis in 50% aqueous potassium hydroxide,[2] was dried under vacuum using phosphorus pentoxide, and was stored under dry nitrogen in a vacuum desiccator. Dibenzhydryl oxalate was prepared by standard procedures.[23] Nitrosonium and nitronium tetrafluoroborate[24] salts were obtained from Ozark-Mahoning Co. and were dried over phosphorus pentoxide in a vacuum desiccator for several hours prior to use. Acetonitrile was distilled from calcium hydride and stored over molecular sieves; nitromethane and benzonitrile were similarly purified prior to use.

Reactions of Azodicarboxylates with Nitrosonium and Nitronium Salts. To a rapidly stirred solution of the nitrosonium or nitronium salt (4.0 mmol) in 3 ml of anhydrous acetonitrile, contained in a three-necked flask fitted with an addition funnel, gas inlet tube, and outlet to a calibrated gas buret, was slowly added the azodicarboxylate (2.0 mmol) in 7 ml of acetonitrile, usually over a 15-min period. Prior to mixing the reactants, the reaction system was thoroughly flushed with dry nitrogen or argon. Reactions were usually run at room temperature, 25 ± 3 °C. Due to its low solubility in aprotic solvents, potassium azodicarboxylate was added as a solid in small portions from a bent addition tube to the nitrosonium or nitronium salt in 10 ml of acetonitrile.

In reactions of nitrosonium or nitronium salts with potassium or di-*tert*-butyl azodicarboxylates, gas evolution commenced upon the initial mixing of the reactants and was rapid and constant throughout the period of addition. However, neither diethyl nor diphenyl azodicarboxylate reacted with $NO^+BF_4^-$ even when the reaction temperature was raised to 60 °C. Diethyl azodicarboxylate was recovered unchanged after treatment with $NO^+BF_4^-$ in acetonitrile for 2 h at room temperature. In contrast, diethyl azodicarboxylate reacted vigorously with $NO_2^+BF_4^-$ in acetonitrile at room temperature.

After gas evolution was complete from reactions of azodicarboxylate esters, an aliquot was removed for ^1H NMR analysis. The *N*-*tert*-butyl- and *N*-ethylacetonitrilonium ions were identified by comparison to the reported spectra of these ions; chemical shifts and coupling constants were identical with those of the reported spectra.[10] The *tert*-butyl group of the *N*-*tert*-butylbenzonitrilonium ion in benzonitrile was observed at δ 1.68. Quenching of the reaction solution with water resulted in the formation of *N*-alkylamides which were identified prior to and after ether extraction by standard methods. Products from the reaction of di-*tert*-butyl azodicarboxylate with $NO^+BF_4^-$ in benzene, *tert*-butylbenzene and di-*tert*-butylbenzene, were analyzed by GLC on a 5-ft 10% SE-30 column; *tert*-butylbenzene was not formed when this same reaction was run in acetonitrile containing a 10 molar excess of benzene over di-*tert*-butyl azodicarboxylate.

Dinitrogen tetroxide was assayed from the yellow acetonitrile solution following the reactions of azodicarboxylates with $NO_2^+BF_4^-$ by the standard method of total acidity.[25] The total yield of N_2O_4 was calculated after correction was made for unreacted $NO_2^+BF_4^-$. The assayed yields were within 2% of those predicted by the stoichiometry of eq 13. Nitrite ion was assayed by standard spectrophotometric methods.[26]

Gas Analyses. The gaseous products evolved in reactions of azodicarboxylates and oxalates with nitrosonium and nitronium salts were collected in a gas buret and their volume was measured by water displacement. Gas samples were taken from the gas buret reservoir for mass spectral ($CO_2 + N_2O$, NO_2, NO, N_2), IR (CO_2, N_2O, NO_2, and NO), and GLC (all gaseous products) analyses. For GLC analyses use was made of 3-ft molecular sieve 5A columns operated at 65 °C for N_2 and NO detection and programed to 220 °C at 20 °C/min for NO_2, N_2O, and CO_2 analyses; the gaseous products were identified by comparison with the retention times of authentic gas samples. The gaseous product mixtures were quantitatively analyzed by GLC with the use of separately measured thermal conductivity ratios, each relative to carbon dioxide. Direct gas sampling was effected from the reaction flask through a 6-port gas sample valve.

Infrared Spectral Studies. The infrared spectra of solutions obtained from reactions between $NO_2^+BF_4^-$ and di-*tert*-butyl azodicarboxylate in anhydrous acetonitrile or nitromethane were obtained at temperatures between −15 and 0 °C. The spectral region between 2200 and 1500 cm^{-1} was recorded for reactions in acetonitrile; that between 2800 and 1600 cm^{-1} was recorded for reactions in nitromethane. Each absorption assigned to **4** was observed to decrease in intensity with time as the reaction solution was warmed from −15 to 0 °C. Comparison was made between the spectra obtained of these reaction solutions and the spectra of azodicarboxylate esters, those of reaction products (CO_2,N_2O, NO, and the *N-tert*-butylacetonitrilonium ion), and the absorptions arising from possible contaminants (particularly N_2O_4). Absorptions similar to those that decreased in intensity in $NO^+BF_4^-$ reactions with di-*tert*-butyl azodicarboxylate were observed in acetonitrile solutions following treatment of diethyl and diphenyl azodicarboxylate with $NO^+BF_4^-$. Due to the apparent low solubility of **4** in nonpolar solvents, comparable absorptions were not detected when the azodicarboxylate esters were added to $NO^+BF_4^-$ in carbon tetrachloride. The reaction between potassium azodicarboxylate with nitrosonium salts was sufficiently rapid at −15 °C that infrared spectral analysis of the reaction intermediate could not be made.

Acknowledgment. Support for this work from the National Science Foundation is gratefully acknowledged.

References and Notes

(1) (a) Part X: Reactions of the Nitrosonium Ion. Part IX: M. P. Doyle, J. L. Whitefleet, and M. A. Zaleta, *Tetrahedron Lett.*, 4201 (1975). (b) Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Awardee, 1973–1978. (c) National Science Foundation Undergraduate Research Participant, Summer 1969 (W.W.), 1972 (D.J.D.), 1975 (J.L.W.).

(2) J. Thiele, *Justus Liebigs Ann. Chem.*, **271**, 127 (1892).

(3) S. Hünig, H. R. Muller, and W. Thier, *Angew. Chem., Int. Ed. Engl.*, **4**, 271 (1965); C. E. Miller, *J. Chem. Educ.*, **42**, 254 (1965).

(4) M. P. Doyle, J. J. Maciejko, and S. C. Busman, *J. Am. Chem. Soc.*, **95**, 952 (1973).

(5) In the presence of water nitrosation of potassium azodicarboxylate gives CO_2, N_2, and N_2O in a molar ratio of 4:2:1. This stoichiometry is suggestive of protonic decomposition of potassium azodicarboxylate to carbon dioxide and diimide, followed by disproportionation of diimide to nitrogen and hydrazine[6] and subsequent nitrosative decomposition of hydrazine to nitrogen and nitrous oxide.

(6) (a) C. V. King, *J. Am. Chem. Soc.*, **62**, 379 (1940); (b) C. V. King and J. J. Josephs, *ibid.*, **66**, 767 (1944).

(7) Decarboxylation of phenylazocarboxylate anions is believed to occur by protonation at the diazene nitrogen,[8] and association of iridium and platinum complexes with diethyl azodicarboxylate is observed to occur at the diazene rather than the carbonyl group.[9]

(8) P. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 2354 (1968).

(9) M. Green and R. B. L. Osborn, *J. Chem. Soc. A*, 3083 (1968).

(10) G. A. Olah and T. E. Kiovsky, *J. Am. Chem. Soc.*, **90**, 4666 (1968).

(11) Unidentified products account for nearly 20% of the reaction products isolated after quenching with water. These products may have resulted from reactions of the nitrosonium ion with isobutylene.

(12) The production of nitrous oxide is not due to hydrolysis of the azodicarboxylate ester followed by nitrosation of diimide or its hydrazine decomposition product. Neither diethyl nor diphenyl azodicarboxylate reacted with $NO^+BF_4^-$ under identical reaction conditions except that reaction times were one hundred times longer than those required for complete decomposition of di-*tert*-butyl azodicarboxylate.

(13) The difference in the standard free energy of formation of N_2O and NO is 4.04 kcal/mol.

(14) The carbonyl stretching frequency for iridium and platinum complexes of diethyl azodicarboxylate occurs at 1609 cm^{-1} [9]

(15) Two-electron oxidations of organic substrates by the nitrosonium ion are well known: (a) M. P. Doyle and W. Wierenga, *J. Am. Chem. Soc.*, **94**, 3896 (1972); (b) M. P. Doyle, M. A. Zaleta, J.E. DeBoer, and W. Wierenga, *J. Org. Chem.*, **38**, 1663 (1973); (c) G. A. Olah and N. Friedman, *J. Am. Chem. Soc.*, **88**, 5330 (1966); (d) P. A. S. Smith and R. N. Loeppky, *ibid.*, **89**, 1147 (1967); (e) E. J. Strojny, R. T. Iwamasa, and L. K. Frevel, *ibid.*, **93**, 1171 (1971).

(16) M. P. Doyle and D. J. DeBruyn, Abstracts, 163d National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972, ORGN-155.

(17) The equilibrium between dinitrogen tetroxide and nitrosonium nitrate in polar solvents is well established: C. C. Addison, *Angew. Chem.*, **72**, 193 (1960).

(18) Nitronium tetrafluoroborate also reacts with sodium oxalate to yield carbon dioxide and dinitrogen tetroxide as the sole products in this rapid transformation.

(19) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds", American Elsevier, New York, N.Y., 1965.

(20) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution—Nitration and Halogenation", Academic Press, New York, N.Y., 1959.

(21) G. A. Olah and H. C. Lin, *J. Am. Chem. Soc.*, **93**, 1259 (1971).

(22) M. P. Doyle and C. T. West, *J. Org. Chem.*, **40**, 3821 (1975).

(23) W. S. Trahanovsky, J. A. Lawson, and D. E. Zabel, *J. Org. Chem.*, **32**, 2287 (1967).

(24) Careful analyses for the nitrosonium ion in nitronium tetrafluoroborate salts were made by gravimetric analyses of the residue obtained after addition of the commercial nitronium tetrafluoroborate salt to benzene and by subsequent volumetric analyses of the gas yield from titration of this residue with urea in acetonitrile. The maximum molar amount of the nitrosonium ion was less than 5% in all determinations.

(25) Hercules, "Nitrogen Tetroxide", Air Products and Chemicals, Inc., Allentown, Pa., 1968.

(26) M. J. Taras, A. E. Greenberg, R. D. Hoak, and M. C. Rand, Ed., "Standard Methods for the Examination of Water and Wastewater", 13th ed, Water Pollution Control Federation, 1971.

Hydrogen Bonding in Organic Synthesis. 3. Hydrogen Bond Assisted Reactions of Cyclic Organic Hydrogen Bond Electron Acceptors[1] with Halogenoalkanes in the Presence of Potassium Fluoride

James H. Clark and Jack M. Miller*

Contribution from the Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1. *Received May 3, 1976*

Abstract: The condensation reactions of a number of cyclic organic compounds, benzoic acid, phenol, 1,2-dihydroxybenzene, *N*-methylaniline, aniline, piperidine, pyrrolidine, phthalimide, and benzene thiol with halogenoalkanes in the presence of potassium fluoride are described. The reactions are thought to be accelerated by the formation of H bonds between the fluoride anion and the cyclic organic electron acceptors. Cesium fluoride in place of KF speeds up the reactions by an order of magnitude. Large shifts in the fundamental stretching vibration of the electron acceptor group have been reported for a number of cyclic organic fluoride systems, indicative of H bonding. Values for the H bond enthalpy of selected systems fluoride–benzoic acid, fluoride–phenol, and fluoride–1,2-dihydroxybenzene (113 ± 5, 60 ± 5, and 63 ± 7 kJ mol^{-1}, respectively) have been predicted on the basis of reported correlations between the H bond enthalpy and the IR shift on H bonding.

The importance of using ionic salts in organic synthesis has been recognized for many years. One of the apparent drawbacks with such applications is that most solvents capable of dissolving both the ionic salt and organic reactants are protic solvents and through H bonding tend to solvate anions particularly strongly, and anions, as bases and nucleophiles, are usually the important half of an ionic reagent. Alkali metal fluorides fall into this category and efforts to apply these salts to organofluorinations have often met with little success. Although it has been recognized that the ineffectiveness of many