graphed along with other products with 30% ethyl acetate/hexane (MPLC). The methyl esters of the lactone acids were prepared by treatment with diazomethane after chromatography.

(3aα,5aα,8a*S)-3,3,6,6-Tetraphenyl-2,7-dioxacyclopenta[*a*]pentalene-1,8-dione (15)**: mp 248–249 °C; IR (KBr) 3080, 3060, 3030, 2970, 2930, 1785, 1763 (strongest $C{=}O$), 1597, 1493, 1448, 1322, 1290, 1270, 1210, 1170, 1150, 1045, 1031, 1015, 998, 975, 757, 697 cm^{-1}; ^{1}H NMR δ 7.60–7.15 (m, 20 H), 4.08 (m, 2 H), 1.70 (m, 2 H), 1.30 (m, 2 H); ^{13}C NMR 171.3, 143.5, 141.5, 128.5, 128.0, 127.5, 125.9, 125.2, 125.0, 90.5, 65.9, 56.6, 32.3; MS exact mass calcd for $C_{33}H_{26}O_4$ m/z 486.1824, found 486.1852.

Hexahydro-6a-carboxy-3,3-diphenyl-6-(diphenylmethylene)-1*H*-cyclopenta[*c*]furan-1-one (17a): IR (KBr) 3420, 3050, 3020, 2955, 2920, 1773, 1730, 1597, 1492, 1450, 1260, 1150, 1090, 1045, 1030, 970, 760, 697 cm^{-1}; ^{1}H NMR δ 7.7–7.1 (m, 20 H), 5.4–5.0 (br s, 1 H), 4.27 (dd, J = 4.6, 7.2 Hz, 1 H), 2.67 (m, 1 H), 2.30 (m, 1 H), 1.88 (m, 1 H), 1.50 (m, 1 H); MS ($m - 44(CO_2))/z$ 442.

Hexahydro-6a-carbomethoxy-3,3′-diphenyl-6-(diphenylmethylene)-1*H*-cyclopenta[*c*]furan-1-one (17a methyl ester): IR (KBr), 3060, 3020, 2950, 1787, 1735, 1595, 1490, 1450, 1255, 1145, 1030, 975, 760, 700 cm^{-1}; ^{1}H NMR δ 7.6–7.1 (m, 20 H), 4.26 (dd, J = 5.8, 7.2 Hz, 1 H), 2.72 (m, 1 H), 2.38 (s, 3 H), 2.32 (m, 1 H), 1.77 (m, 1 H), 1.35 (m, 1 H); MS exact mass calcd for $C_{34}H_{28}O_4$ m/z 500.1988, found 500.2006.

Hexahydro-3,3-diphenyl-6-(diphenylmethylene)-1*H*-cyclopenta[*c*]furan-1-one (18a − H_2O): mp 226–226.5 °C; IR (KBr) 3085, 3060, 3025, 2955, 2922, 1766, 1598, 1495, 1450, 1443, 1242, 1213, 1190, 1152, 1090, 965, 935, 758, 698 cm^{-1}; ^{1}H NMR δ 7.65–7.10 (m, 10 H), 3.79 (dt, J = 6.7, 8.0 Hz, 1 H), 3.66 (d, J = 6.8 Hz, 1 H), 2.50 (dt, J = 8.8, 17.6 Hz, 1 H), 2.32 (ddd, J = 3.7, 10.1, 17.6 Hz, 1 H), 1.78 (m, 1 H), 1.50 (m, 1 H); MS calcd for $C_{32}H_{26}O_2$ m/z 442.1934, found 442.1932.

(3aα,5aβ,8a*S)-3,3,6,6-Tetramethyl-2,7-dioxacyclopenta[*a*]pentalene-1,8-dione (16)**: mp 178.5–179 °C; IR (KBr) 2983, 2950, 1770, 1743 (strongest $C{=}O$) 1450, 1388, 1312, 1268, 1233, 1185, 1168, 1142, 1100, 1022, 960, 907 cm^{-1}; ^{1}H NMR δ 2.9–2.8 (m, 2 H), 2.1–1.9 (m, 2 H), 1.80–1.55 (m, 2 H), 1.70 (s, 6 H), 1.42 (s, 6 H); ^{13}C NMR 173.2, 85.0, 67.4, 57.0, 30.5, 30.3, 23.8 (57.0, 30.3, and 23.8 are negative with Attached Proton Test and therefore bear an odd number of hydrogens); MS exact mass calcd for $C_{13}H_{18}O_4$ 238.1205, found 238.1205.

Acknowledgment. We are indebted to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. (±)-**4s-s**, 94842-23-6; (±)-**4u**, 94842-24-7; (±)-**4s-a**, 94842-25-8; (±)-**5s-s**, 94842-26-9; (±)-**5u**, 94842-27-0; (±)-**5s-a**, 94842-28-1; (±)-**6s-s**, 94800-14-3; (±)-**6u**, 94842-29-2; (±)-**6s-a**, 94842-30-5; (±)-**7s-s**, 94842-31-6; (±)-**7u**, 94842-32-7; (±)-**7s-a**, 94902-02-0; (±)-**8s-s**, 94842-33-8; (±)-**8u**, 94842-34-9; (±)-**8s-a**, 94842-35-0; **9**, 89536-28-7; **10**, 55775-73-0; **11**, 4372-10-5; **12**, 89536-31-2; **13**, 89615-14-5; (±)-**14u**, 94800-15-4; (±)-**14s-a**, 94842-36-1; **15**, 94800-16-5; **16**, 94800-19-8; (±)-**17a**, 94800-17-6; (±)-**17a** (methyl ester), 94800-21-2; (±)-**17b**, 94800-20-1; (±)-**17b** (methyl ester), 94800-22-3; $CH_3(CH_2)_3CH{=}CH_2$, 592-41-6; $CH_3(CH_2)_5CH{=}CH_2$, 111-66-0; $(CH_3)_3CCH{=}CH_2$, 558-37-2; $PhC(CH_3){=}CH_2$, 98-83-9; $ClCH_2CH{=}CH_2$, 107-05-1; $Ph_2C{=}CH_2$, 530-48-3; $(CH_3)_2C{=}CH_2$, 115-11-7; $CH_2{=}CH_2$, 74-85-1; $Ph_2C{=}CH(CH_2)_2CH{=}CPh_2$, 70671-93-1; $(CH_3)_2C{=}CH(CH_2)_2CH{=}C(CH_3)_2$, 16736-42-8; $Mn(OAc)_3$, 993-02-2; $CH_2(CO_2H)_2$, 141-82-2; (±)-*cis*-hexahydro-3,3-diphenyl-6-(diphenylmethylene)-1*H*-cyclopenta[*c*]furan-1-one, 94800-18-7; methylenecyclohexane, 1192-37-6; cyclohexene, 110-83-8; cyclopentene, 142-29-0.

Thermolysis of Molecules Containing NO_2 Groups[1]

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MINDO/3 calculations are reported for the thermal decomposition of nitromethane, methyl nitrite, methyl nitrate, nitroethylene, 1,1-dinitroethylene, *cis*-1,2-dinitroethylene, tetranitroethylene, nitroacetylene, and dinitroacetylene. The nitro compounds decompose most easily by first rearranging to isomeric nitrites. Methyl nitrite and methyl nitrate can decompose by fission into radicals ($CH_3O\cdot$ + $\cdot NO$ or $\cdot NO_2$) or by alternative routes involving cyclic elimination ($CH_3ONO \rightarrow CH_2O + HONO$) or intermolecular transfer of oxygen ($CH_3ONO_2 + HCH_2ONO_2 \rightarrow CH_3ONO + HOCH_2ONO_2$). In the case of methyl nitrate, the latter alternative is likely to be favored under the conditions of a detonation shock wave. The activation energies calculated for the nitro → nitrite rearrangements of tetranitroethylene and of dinitroacetylene suggest that neither will be thermally stable.

Introduction

Reactions involving the thermolytic cleavage of bonds to form pairs of radicals have been extensively studied in recent years, partly because of their interest in connection with theories of unimolecular reactions and partly as a source of information concerning the heats of formation of radicals and bond dissociation energies (BDE). It is generally assumed that radical combination normally takes place without activation. If so, the observed activation energy for a bond dissociation process is equal to the BDE, while the heats of formation of the radicals formed are equal to that of the parent molecule *plus* the BDE.

Compounds containing the NO_2 group have been of especial interest in this connection, partly because they undergo thermal decomposition at relatively low temperatures and partly because of the role such decompositions play in the detonation of explosives. The activation energies for decomposition into radicals are moreover expected to be low because of the exceptional stability of nitric oxides ($\cdot NO$) and nitrogen dioxide ($\cdot NO_2$). The easy

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[1] Part 65 of the series "Ground State of Molecules". Part 64: Dewar, M. J. S.; Healy, E. *J. Comp. Chem.* **1983**, *4*, 542.

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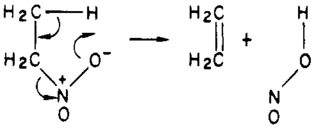
thermal decompositions of the three main classes of NO_2-containing species, i.e., alkyl nitrites (**1**), alkyl nitrates (**2**), and nitro compounds (**3**), have therefore been commonly assumed to take place by the following routes:

$$\underset{\mathbf{1}}{RONO} \rightarrow RO\cdot + \cdot NO \quad (1)$$

$$\underset{\mathbf{2}}{RONO_2} \rightarrow RO\cdot + \cdot NO_2 \quad (2)$$

$$\underset{\mathbf{3}}{RNO_2} \rightarrow R\cdot + \cdot NO_2 \quad (3)$$

The activation energies observed for the thermal decompositions of such compounds have, however, tended to be uniformly less than the BDEs estimated for the relevant bonds independent determinations of the heats of formation of the corresponding alkoxy (RO·) and alkyl (R·) radicals. While recent work[3] indicates that the discrepancy in the case of alkyl nitrites (**1**) was due to interfering chain reactions in the earlier experiments, and while the formation of ethylene during the thermolysis of nitroethane (**4**) suggests[4] that this reaction takes place by a cyclic elimination of nitrous acid (eq 4), the discrepancies otherwise remain to be explained. Theoretical calculations, using MINDO/3[5] or MNDO,[6] have proved useful in many other cases where problems of this kind have arisen and we therefore decided to try them here. We have accordingly carried out an extensive study of the decompositions of a number of compounds containing the NO_2 groups by using MINDO/3. While MNDO is usually better than MINDO/3, compounds containing the NO_2 groups are among the exceptions. While MINDO/3 reproduces their heats of formation in a satisfactory manner, the MNDO values are subject to unusually large errors. As will appear presently, our work has led not only to a solution of the problems indicated above but also to some novel and interesting mechanistic predictions.



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(4)

Procedure

The calculations were carried out by using the standard MINDO/3 procedure and parameters.[5] Systems involving radicals were studied by using the spin-unrestricted version of MINDO/3 (UMINDO/3). Geometries were calculated by minimizing the energy with respect to all geometrical variables, using the gradient method incorporated in the MOPAC[7] package of computer programs, and making no assumptions. Transition states were located by using a suitable geometrical variable as a reaction coordinate[8] and refined by minimizing the norm of the energy.[9] Stationary points were characterized by checking the number of negative eigenvalues of the Hessian (force constant) matrix.[9]

Table I. Calculated and Observed Heats of Formation (kcal/mol)

species	UMINDO/3	obsd[a]
CH_3	41.0	34.0
CH_3O	4.0	3.9
NO	21.1	21.6
NO_2	25.3	8.1
CH_3ONO	14.5	15.6
CH_3ONO_2	28.3	29.1
CH_3NO_2	10.4	17.0

[a] Reference 4.

Molecular vibration frequencies were calculated in the usual way[10] and used, together with moments of inertia derived from the calculated geometries, to determine partition functions and hence molecular entropies.[11]

MINDO/3 leads to estimates of heats of formation. The difference between the heats of formation of the reactants and the transition state (TS) in a reaction, i.e., the heat of activation ($\Delta H^{\ddagger}$), differs from the Arrhenius activation energy (AAE), the relation between them being

$$AAE = \Delta H^{\ddagger} + RT \quad (5)$$

Likewise the Arrhenius preexponential factor (APF) is given in terms of the entropy of activation ($\Delta S^{\ddagger}$) by

$$APF = (kT/h) \exp(\Delta S^{\ddagger}/R) \quad (6)$$

AAEs and APFs were calculated by using eq 5 and 6.

Several authors have recently claimed that ab initio SCF MO treatments fail to reproduce compounds containing the NO_2 group adequately unless configuration interaction (CI) is included. These arguments do not, however, apply to the procedures developed here, for reasons discussed in the Appendix.

Results and Discussion

A. Tests of MINDO/3. The first objective in any theoretical study should be to test the procedure that is to be used in the specific area in which one is about to use it. This applies equally to *all* procedures, ab initio as well as parametric. We therefore began by calculating the heats of formation of various molecules and radicals that are, or might be, implicated in the thermal decompositions of nitromethane (**5**), methyl nitrite (**6**), and methyl nitrate (**7**). The results are compared with experiment in Table I.

CH_3NO_2 **5** CH_3ONO **6** CH_3ONO_2 **7**

The agreement is good except for nitrogen dioxide, where the error is not unexpected.[5] Since two-center integrals involving one-center overlap are neglected in MINDO/3, MINDO/3 fails to reproduce hybridization moments. The repulsions between electrons occupying hybrid AOs of adjacent atoms are consequently underestimated. The heats of formation calculated by MINDO/3 for molecules where adjacent atoms have electrons localized in hybrid AOs are consequently much too negative.[5] Nitrogen dioxide is a typical example. The repulsions (**8**) between the unshared electron, which occupies a hybrid nitrogen AO, and the unshared pairs of electrons on the oxygen atoms, are underestimated, so the calculated heat of formation is too negative. No problems arise in the case of nitro compounds or nitrates, or indeed in NO_2^+, because the nitrogen atoms in them have no unshared valence electrons. It may seem surprising that similar errors do not appear for nitric oxide and methyl nitrite. The rele-

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(3) Batt, L.; Milne, R. J. *Int. J. Chem. Kinet.* **1974**, *6*, 945. Batt, L.; Islam, T. S. A.; Scott, H. *Ibid.* **1978**, *10*, 1175.

(4) Spokes, G. N.; Benson, S. W. *J. Am. Chem. Soc.* **1967**, *89*, 6030.

(5) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307.

(6) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

(7) Available from QCPE in versions for DEC VAX, CDC, and IBM computers.

(8) See Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1971**, *93*, 4290.

(9) (a) McIver, J. W., Jr.; Komornicki, A. *Chem. Phys. Lett.* **1971**, *10*, 303. (b) McIver, J. W., Jr.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2623. (c) McIver, J. W., Jr. *Acc. Chem. Res.* **1974**, *7*, 72.

(10) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1685.

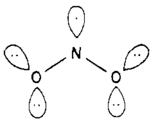
(11) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 7822.

Table II. Calculated and Observed Bond Strengths (kcal/mol)

bond	calcd	obsd[a]
CH_3–NO_2	59.5	60.0
CH_3O–NO	39.6	41.1
CH_3O–NO_2	40.4[b]	42.1

[a] See Table I. [b] Using the experimental heat of formation for NO_2; see text.

vant dipole–dipole repulsions depend critically, however, on the hybridization of the AOs involved and their angular orientation and distances apart. Since the NO parameters in MINDO/3 provide a global average correction for the neglected repulsions, the error can vary from one molecule to another. The neglected repulsions are likely to be unusually large in NO_2 because of the large number of lone pair interactions.



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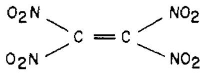

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$O_2N-C\equiv C-NO_2$

11

$O_2N-CH=CH_2$

12

The results in Table I suggest that no problems should arise for any of the other compounds studied. The agreement between the calculated and observed heats of formation for all the other compounds is indeed unusually good. The same should also be true for the transition state (TS) of a reaction in which NO_2 is being eliminated, because the AO which is singly occupied in NO_2 is still being used for bonding in the TS. However, in estimating heats of reaction for processes where NO_2 is a reactant or product, it is clearly necessary to use the experimental value for its heat of formation rather than the calculated (MINDO/3) value. As Table II shows, the bond dissociation energies (BDE) calculated in this way for dissociation of molecules (XNO_2) into radicals ($X\cdot + \cdot NO_2$) agree well with those deduced from experiment, most of the differences being within the limits of error of the experimental values and all within the limits expected[5] for MINDO/3.

Several authors have recently claimed, on the basis of ab initio calculations, that compounds containing the NO_2 group cannot be adequately represented by single configuration wave functions. This, however, has no bearing on the situation in MINDO/3. Changes in electron correlation play a major role in chemical bonding. These are neglected in the Hartree Fock (HF) approximation and hence in ab initio SCF procedures. The latter can therefore give satisfactory estimates of heats of reaction or activation only when the correlation energies of the reactants and products, or reactants and transition state, are the same. If they are not the same, inclusion of configuration interaction (CI) may improve the situation by providing a partial allowance for the effects of electron correlation. In MINDO/3, however, electron correlation is taken implicitly into account via the parametrization. The fact that ab initio methods fail for compounds of some specific type does not therefore imply that MINDO/3 will likewise fail or even encounter difficulties.

It should be remembered that the errors in heats of atomization, calculated for organic molecules by ab initio procedures close to the HF limit, are very large, usually ca 30%. Thus the error in the 6-31G* energy for benzene is 650 kcal/mol, the corresponding heat of atomization being 1320 kcal/mol.[12] Significant random fluctuations might be expected in the errors for different molecules and recent work[12] suggests that these can in fact be large, even for small molecules and even using a large basis set. For example, the errors for carbon dioxide and formic acid, using the 6-31G* basis set, are 15.7 and 12.9 kcal/mol, respectively.[12] Compounds containing the NO_2 group apparently represent such a random fluctuation. They certainly do not exhibit any special features (e.g., biradical character) which would be expected to invalidate their treatment by the standard RHF version of MINDO/3.

As a check, we also calculated nitromethane with three open shell MINDO/3 procedures, i.e., the UHF version (UMINDO/3), a version including CI (MINDO/3-CI), and a version (MINDO/3 HE) using the "half electron" approximation. In the case of biradicals, the energies given by these are more negative than those from MINDO/3 by ~40 kcal/mol. The results obtained were as follows:

MINDO/3	−10.40 kcal/mol
UMINDO/3	−10.40 kcal/mol
MINDO/3-CI	−12.15 kcal/mol
MINDO/3-HE	−5.75 kcal/mol

Nitromethane is clearly predicted to have *no* biradical character.

The results obtained from MINDO/3 studies of the decomposition of various molecules containing the NO_2 group follow.

B. Nitromethane (5). The experimental heats of formation listed in Table I lead to a value of 60.0 kcal/mol for the BDE of the C–N bond in nitromethane (**5**).

$$CH_3NO_2 \rightarrow H_3C\cdot + \cdot NO_2 \qquad \Delta H = 60.0 \text{ kcal/mol} \qquad (7)$$

From the kinetics of the reverse reaction, O'Neal and Benson[13] arrived at the following activation parameters:

$$\text{AAE} = 59.0 \text{ kcal/mol} \qquad \log_{10} \text{APE} = 15.6 \qquad (8)$$

The experimental activation energies reported[4,14,15] for the thermolysis of **5** have been much less than this, ranging as low as 42.8 kcal/mol. The first step in the decomposition of **5** cannot therefore be a simple dissociation into radicals (eq 4). Nor can it involve a cyclic elimination, because no such elimination can lead to products with energies low enough for the overall AAE to be less than 60 kcal/mol. Decomposition into nitrous acid and carbene, even triplet carbene, would, for example, be much more endothermic than this.[16] The only remaining alternative is a molecular rearrangement of some kind. Indeed, it has often been suggested in the past, though without any real evidence, that nitro compounds (**1**) and isomeric nitrites (**2**) may be thermally interconvertable. Since the AAE for decomposition of methyl nitrite (**6**) is quite low (see below), facile rearrangement of nitromethane (**5**) to **6** would account for the low AAE observed for the thermolysis of **5**.

$$H_3CNO_2 \rightarrow H_3CONO \rightarrow H_3CO\cdot + \cdot NO_2 \qquad (9)$$

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[12] Dewar, M. J. S.; Storch, D. M. Unpublished results.

[13] O'Neal, H. E.; Benson, S. W. "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NB521, Washington, D.C., 1970.

[14] Borisov, A. A.; Kogarko, S. M.; Shachov, G. I. *Kinet. Katal.* **1966**, *7*, 521.

[15] Smith, T. E.; Calvert, J. G. *J. Phys. Chem.* **1959**, *63*, 1305.

[16] The MINDO/3 (observed) heats of formation for nitrous acid and triplet carbene (CH_2) are −13.6 (−18.8) and CH_2 91.5 (93) kal/mol. The heat of reaction for its formation from **5** is thus 89 (95) kcal/mol.

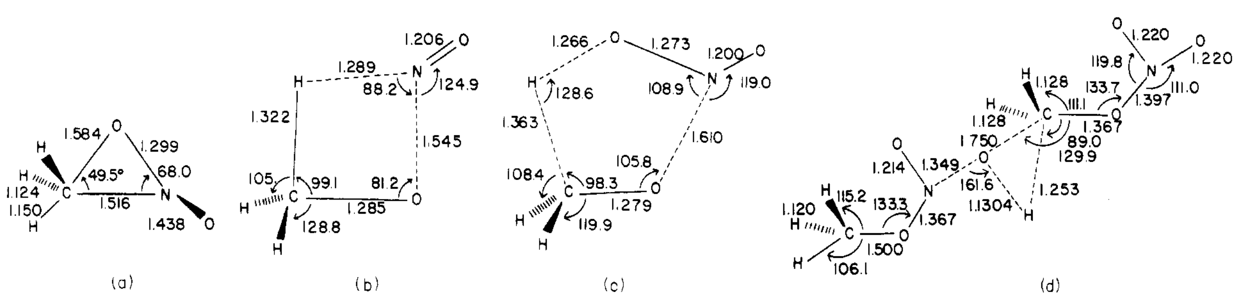


Figure 1. Geometries (bond lengths in Å) calculated for transition states for the conversions: (a) **5** → **6**; (b) **6** → CH_2O + HNO; (c) **7** → CH_2O + HONO; (d) **7** + **7** → **6** + **9**.

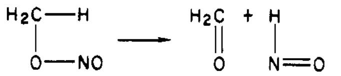
We therefore studied this rearrangement; taking one of the CNO angles (θ) in **5** as the reaction coordinate led to a smooth MERP (minimum energy reaction path) with a maximum at $\theta = 69°$. This structure was refined and characterized as the TS for conversion of **5** to **6** by minimizing the norm of the energy[9] and calculating force constants.[9] Its geometry is shown in Figure 1a and the calculated activation parameters in eq 10.

$$\Delta H = 47.0 \text{ kcal/mol} \qquad \Delta S = -3.6 \text{ eu} \qquad (10)$$

$$\text{AAE} = 47.6 \text{ kcal/mol} \qquad \log_{10} \text{APF} = 13.3$$

The ratio of the rate of rearrangement of **5** to **6** (eq 9) to that of decomposition into radicals (eq 7) can be estimated from the Arrhenius parameters in eq 7 and 10. Its value at 700 °C, a temperature in the range used in most of the experimental studies, is 17:1, implying that almost all the thermolysis takes place via rearrangement to **6**. Indeed, our calculated activation parameters for the latter (eq 10) agree quite well with most of the more recent ones derived from rates of thermolysis, the reported activation energies for the latter ranging from 49.2 to 53.6 kcal/mol and the values for $\log_{10}$ APF from 13.4 to 14.6. Fission into radicals should become more important at higher temperatures with a corresponding increase in the observed activation energy. It is interesting to note that Borisov et al.[14] obtained higher values for the activation energy (57 kcal/mol) and for $\log_{10}$ APF (15.1) in a study of the reaction in a shock tube at higher temperatures (700–1300 °C).

C. Methyl Nitrite (6). A significant difference was once thought to exist between the activation energies (~37 kcal/mol) reported[17-19] for the thermal decomposition of methyl nitrite (**6**) and the value (41.1 kcal/mol) estimated by O'Neal and Benson[21] for the MeO–NO BDE. It was suggested[17-19] that **6** may decompose more easily by an intramolecular elimination rather than by fission into radicals. As noted above, recent work[2] suggests that the


(11)

$$\begin{matrix} H_2C\text{—}H \\ | \\ O\text{—}NO \end{matrix} \longrightarrow \begin{matrix} H_2C & + & H \\ \| & & | \\ O & & N{=}O \end{matrix} \qquad (11)$$

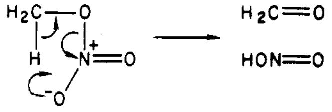
discrepancy was in fact due to participation by chain reactions in the earlier studies, the true unimolecular decomposition having an activation energy close to that estimated by O'Neal and Benson.[13] However, since the new measurements[2] were carried out only for some higher alkyl nitrites, not for **6**, and since the suggested alternative (eq 11) is in any case of interest in itself, we decided to study it. Note incidentally that it is *not* "forbidden" in spite of its superficial resemblance to analogous dissociations which are forbidden, e.g., that of cyclobutane to ethylene, because the nitrogen atom in **6** can use different AOs to bond to oxygen and hydrogen in the TS. The conjugated system in the TS is thus cruciconjugated,[20] i.e., effectively linear, like that in the TS for hydroboration of an olefin.[20,21]

Locating the TS for the rearrangement proved surprisingly difficult. We finally succeeded only by a two-dimensional grid search using the lengths of the CN and NH bonds as the reaction coordinates. The TS found in this way was refined by minimizing[9] the norm of the energy and characterized by calculating force constants.[9] Its calculated geometry is shown in Figure 1b. The calculated entropy and heat of formation led to values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 32.4 kcal/mol and −7.5 eu, respectively, and hence to the following Arrhenius parameters.

$$\text{AAE} = 33.0 \text{ kcal/mol} \qquad \log_{10} \text{APF} = 11.5 \qquad (12)$$

Clearly this mechanism cannot be ruled out as unreasonable. Indeed, the rate constant calculated from it at 500 °C is almost the same as that given by the parameters (AAE = 41.1 kcal/mol, $\log_{10}$ APF = 15.6) deduced by O'Neal and Benson[13] for dissociation into radicals (eq 2). It would be interesting to see if the rates of decomposition at lower temperatures deviate from the corresponding Arrhenius plot.

D. Methyl Nitrate (7). Here again there is a discrepancy between the activation energies reported[13,22] for the thermolysis of methyl nitrate (**7**) and the value (39.8 kcal/mol) estimated from thermochemical data (Table I) for the BDE of the $O\text{–}NO_2$ bond (cf. eq 2). O'Neal and Benson[13] suggested that the thermolysis might take place by a kind of retroene reaction rather than by dissociation.



(13)

We therefore studied this reaction by using MINDO/3. We found the corresponding TS without difficulty; its calculated geometry is shown in Figure 1c. The corresponding AAE (56.5 kcal/mol) was, however, far larger than the activation energies observed for the thermolysis of **7** or estimated for its dissociation into radicals. The difference is indeed so large that the possibility of intervention by this process can be ruled out.

An alternative possibility was suggested some years ago by Alster (see Alster et al.[23]) on the basis of preliminary MINDO/3 calculations. These suggested that **7** can undergo an unprecedented bimolecular oxidation–reduction

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(17) Phillips, L. *J. Chem. Soc.* **1961**, 3082.

(18) Levy, J. B. *J. Am. Chem. Soc.* **1956**, *78*, 1780.

(19) Steacie, E. W. R.; Shaw, G. T. *J. Am. Chem. Soc.* **1935**, *3*, 344.

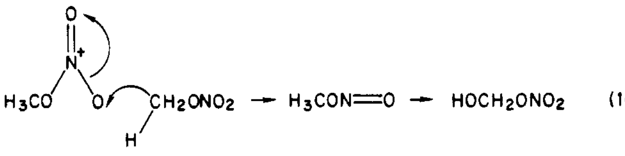
(20) Dewar, M. J. S.; McKee, M. L. *J. Am. Chem. Soc.* **1978**, *100*, 7499.

(21) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978**, *17*, 1075.

(22) Appin, A.; Chariton, J.; Todes, O. *Acta Physicochim. URSS* **1936**, *5*, 655.

(23) Alster, J.; Slag, N.; Dewar, M. J. S.; Ritchie, J. P.; Wells, C. C. "Internationale Jahrestagung 1979; Combustion and Detonation Processes"; Fraunhufer Institut für Treff und Explosivstoffe: Karlsruhe, West Germany, 1979.

process, involving insertion of an oxygen atom from the nitro group of one molecule of **7** into a CH bond of the other.


(14)

7 **7** **6** **9**

Since **6** is known to decompose faster than **7**, and since **9** should do likewise being the hemiacetal from formaldehyde and nitric acid, this reaction provides a viable alternative mode of decomposition. The estimated activation energy was moreover less than the BDE for fission of **7** into radicals (cf. eq 3). We have now fully confirmed these conclusions. Figure 1d shows the geometry calculated for the TS and eq 15 the calculated activation parameters. The value of $\Delta H^{\ddagger}$ is much less than the relevant BDE.

$$\Delta H^{\ddagger} = 32.3 \text{ kcal/mol} \qquad \Delta S^{\ddagger} = -34.7 \text{ eu} \qquad (15)$$

The experimental studies were, however, carried out in the gas phase where the low concentration of **6** would favor the unimolecular dissociation (eq 3) over the bimolecular reaction of eq 14. The dissociation should also involve a large increase in entropy, all of which should appear in the entropy of activation if, as is likely, recombination of the radical products ($CH_3O\cdot + \cdot NO_2$) takes place without activation. Indeed, the Arrhenius parameters recommended by O'Neal and Benson[13] (eq 16) include an unusually large preexponential factor. The rates of the two reactions

$$\text{AAE} = 39.8 \text{ kcal/mol} \qquad \log_{10} \text{APF} = 15.5 \qquad (16)$$

under the conditions used in the experimental studies, calculated by using the parameters in eq 15 and 16, are comparable with dissociation predominating. As expected on this basis, the observed AAE lay between the values calculated for the two alternative processes but nearer to that for dissociation.

The bimolecular reaction (eq 14) should naturally be favored by an increase in concentration, in particular by passage from the gas phase to a condensed phase. Furthermore, since the volume of activation of a bimolecular reaction is negative while that of a unimolecular dissociation is positive, high pressures should also favor bimolecular decomposition of **7**. Indeed, using the parameters in eq 15 and 16 and volumes of activation derived from the calculated structures together with estimates[23] of the pressure (60 kbar) and temperature (800 °C) associated with a shock wave of sufficient strength to initiate detonation in **7**, we conclude that under these conditions the bimolecular reaction of eq 14 should be 10^7 times faster than bond dissociation (eq 3). Since the bimolecular reaction (eq 14) is also calculated to be strongly exothermic ($\Delta H = -33.5$ kcal/mol), processes of this kind seem likely to be involved in the detonation of nitrate explosives in general. The increase in rate with pressure would moreover account nicely for their sensitivity to shock.

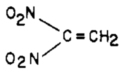
E. Nitroethylenes and Nitroacetylenes. While little is known concerning the chemistry of polynitroethylenes or nitroacetylenes, compounds of this kind are of potential value as synthetic reagents. Those with numerous nitro groups, in particular tetranitroethylene (**10**) and dinitroacetylene (**11**), should moreover be phenomenally powerful electron acceptors and might also serve as precursors to polymers or copolymers of potential value in explosives technology. No synthesis of **10** or **11** has yet been reported[24] and no general methods are known that could be used to prepare them. Attempts to develop new routes would be greatly facilitated by foreknowledge of their properties, in particular their thermal stabilities. If these are low, it would be pointless to try to make them by reactions requiring high temperatures.

Table III. Calculated Heats of Formation[a] (ΔH_f) of Unsaturated Nitro Compounds and Nitrites and Heats of Reaction[a] (ΔH) and Activation[a] (ΔH) for Their Interconversion

R	ΔH_f R-NO_2	ΔH_f R-ONO	ΔH	ΔH
CH_3	10.4	14.5	4.1	47.0
$H_2C{=}CHC$	3.0	0.5	2.5	33.9
$H_2C{=}C(NO_2)$	17.8	15.8	2.0	39.9
cis-$O_2NCH{=}CH$	12.3	21.0	8.7	19.9
$(O_2N)_2C{=}C(NO_2)$	44.5	65.6	21.1	21.5
$HC{\equiv}C$	26.6	32.2	5.6	34.1
$F_3CC{\equiv}C$	156.1	162.4	6.3	23.9
$O_2NC{\equiv}C$	0.3	5.6	5.9	20.0

[a] In kcal/mol.

The arguments above (see B) indicate that the thermal decomposition of nitromethane (**5**) takes place by a preliminary rearrangement to methyl nitrite (**6**) rather than by dissociation into radicals (see eq 1). The same should be true a fortiori for nitroethylenes or nitroacetylenes because the BDE of a σ bond is greater, the greater the s character of the AOs used to form it, and because unsaturated groups usually migrate more easily than saturated ones. We therefore carried out MINDO/3 calculations for **10**, **11**, nitroethylene (**12**), 1,1-dinitroethylene (**13**), *cis*-1,2-dinitroethylene (**14**), and nitroacetylene (**15a**) and for their rearrangements to the isomeric nitrites. The heats of formation of the nitro compounds and nitrites, and the activation energies and heats of reaction for conversion of the former to the latter, are shown in Table III. Values for **5** are included for comparison.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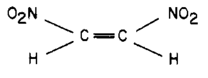
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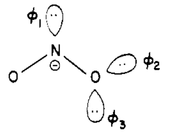
$O_2N{-}C{\equiv}C{-}R$

15 a, R=H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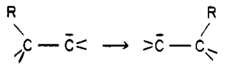
17 18

The activation energies for the rearrangements of **12** and **15a** are, as expected, less than that for **5**. The differences are, however, small. The same is true for **13**, where both nitro groups are attached to the same carbon atom. Dramatic changes occur, however, in compounds containing nitro groups at both ends of a C=C or CC bond. The activation energies for rearrangement are halved by introduction of the extra nitro group(s) and the overall reactions also become very much less endothermic.

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(24) While the Diels–Alder adduct from **11** and anthracene was reported[25] some years ago by Griffin and Baum,[25] attempts to recover **11** from it had failed. We understand from Dr. Baum that **11** has now been obtained from it as a white powder decomposing at 60 °C.

(25) Griffin, T. S.; Baum, K. *J. Org. Chem.* **1980**, *45*, 2880.

Since the calculations reported not only agree well with the available experimental data but also provide satisfactory interpretations of them, there seems no reason to doubt conclusions drawn from MINDO/3 for nitro compounds of other types, in particular the prediction that both **10** and **11** will prove to be rather labile species decomposing at quite low temperatures. While **11** has not yet been reported, we understand from Dr. Baum that **10** has now been obtained from its adduct with anthracene[24] as a white powder, decomposing above 60 °C.

The sensitivity of an explosive to shock most likely depends on the ease with which the primary reaction occurs on initiation of detonation. In the case of a nitro compound, our calculations indicate that the primary reaction is a rearrangement to the corresponding nitrite, that the nitro → nitrite rearrangement should occur more easily in unsaturated nitro compounds than in saturated ones, and that it should be facilitated by electron-withdrawing substituents at positions of opposite parity[26] to the nitro group. Electron-releasing substituents should exert a corresponding stabilizing effect. Nitro paraffins are indeed less easily detonated than unsaturated or aromatic analogues, while amino groups are known to decrease the impact sensitivity of 1,3,5-trinitrobenzene[27] or 2,4,6-trinitrotoluene.[28] Conversely, according to a recent report,[29] hexanitrobenzene decomposes quite rapidly in solution at moderate temperatures, apparently by rearrangement to an unstable nitrite.

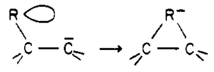
Implications of the Proposed Mechanisms of Decomposition. Our calculations have led to the postulation of novel reactions in the thermal decompositions of nitro compounds and of methyl nitrate. Both raise points of general interest.

(a) The NO_2 Group as an Oxygen Donor. While the chemistry of nitrate esters has been somewhat neglected, for obvious reasons, the work reported here suggests that such compounds may act generally as sources of oxygen atoms for insertion into CH bonds. Since a nitrate ester can be regarded as a nitro derivative of an alcohol, nitro compounds in general might be expected to behave in the same way. This could explain the curiously ambivalent behavior of nitro compounds as oxidizing agents. Thus while nitrobenzene has been used since the early days as an oxidizing agent in organic chemistry (cf. the Skraup reaction) and while it is easily reduced by sources of atomic hydrogen or electrons, it is surprisingly resistant to metal hydrides, and nitro compounds have so far been deoxygenated only by very powerful oxygen acceptors, e.g., phosphines.

(b) Orbital Analysis of the Nitro → Nitrite Rearrangement. The evidence presented here indicates that the interconversion of nitro compounds and nitrites can take place by a normal synchronous 1,2-migration of the group attached initially to nitrogen, the activation energy being, however, much greater than those observed for typical σ-complex-type rearrangements. This is an interesting reaction, as the following discussion shows.

A given nitro compound (**3**) and the isomeric nitrite (**1**) can be derived from a nitrite anion (**16**) by adding R^+ to a nitrogen (ϕ_1) or oxygen (ϕ_2 or ϕ_3) lone pair, the σ MOs remaining basically unchanged. Conversion of **3** to **1** is therefore analogous to the Wagner–Meerwein-like rearrangement of a carbanion (**17** → **18**) and is likewise "forbidden", each reaction involving a cyclic TS isoconjugate with the antiaromatic cyclopropenyl anion. Our calculations nevertheless predict the nitro → nitrite reaction to take place in a normal synchronous manner with a high, but not excessively high, activation energy. While there is no reason[30] why a "forbidden" reaction should not take place in this way, ones which do are rare[32] because there are usually easier alternatives, either a nonsynchronous reaction leading to the same products or some other reaction which is "allowed". The fact that the reaction is "forbidden" is indicated by its relatively high activation energy, this being much greater than those observed for analogous "allowed" rearrangements, e.g., Wagner–Meerwein rearrangements of carbenium ions.

While the rearrangement of **3** to **1** is "forbidden" if R has only a single AO available for bonding to N or O in **16**, this is no longer true if R has a second empty AO. If it has, this can be used to form a σ bond to the adjacent atom directly, without interfering with the existing σ bond to R; cf. **19** → **20**. Thus while the interconversion of nitroparaffins and alkyl nitrites is a difficult "forbidden" process, the analogous interconversion of nitroboranes and boryl nitrites (**21** → **22**) should be very facile. Compounds of this type do not seem to have been reported as yet. The rearrangement of **3** should also be facilitated if R has a low energy π MO available to form an acceptor bond to the adjacent oxygen lone pair (ϕ_2 in **17**). This explains the large rate enhancements predicted in cases where R is a β-nitrovinyl or nitroethynyl group.



19 20

$R_2B\text{-}NO_2 \rightarrow R_2B\text{-}ONO$

21 22

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(26) In an alternant[26] conjugated system, the conjugated atoms can be divided into two sets, starred and unstarred, such that atoms of the same set are not directly linked to one another. Atoms belonging to the same set are said to be of like parity, atoms of different sets of opposite parity. See: Dewar, M. J. S.; Dougherty, R. C. "The PMO Theory of Organic Chemistry"; Plenum Publishing Corp.: New York, 1975.

(27) Ayres, J. N.; Montesi, L. J.; Bauer, R. J. "Small Scale Gap Test Data Compilation"; Naval Ordnance Laboratory Technical Report, 1973; Vol. 1, p 73–132.

(28) Iyer, S. *Propellants Explos.* **1982**, *7*, 37.

(29) Neilsen, A. T.; Norris, W. P.; Atkins, R. L.; Buono, W. R. *J. Org. Chem.* **1983**, *48*, 1056.

(30) This point was immediately obvious in Evans' original formulation[31] of the principles now generally described as the Woodward–Hoffmann rules. If a TS is aromatic or antiaromatic, this leads to a corresponding stabilization or destabilization, which contributes to the corresponding activation energy. There is no reason why a reaction should not take place in a normal synchronous manner if it involves an antiaromatic TS, i.e., if it is "forbidden" by the Woodward–Hoffmann rules. It will indeed do so if there is no better alternative. Aromaticity/antiaromaticity is only one of the factors that determine the energy of a TS.

(31) Evans, M. G. *Trans. Faraday Soc.* **1939**, *35*, 824.

(32) Another example is the "forbidden" conversion of bicyclo[2.1.0]pentene to cyclopentadiene by disrotatory electrocyclic ring opening; see: Dewar, M. J. S.; Kirschner, S. *J. Chem. Soc., Chem. Commun.* **1975**, 461.