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An INDO-MO Study of Peroxyacetyl Nitrate Formation

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Synopsis. The process of peroxyacetyl nitrate (PAN) formation has been disscussed on the basis of INDO calculations. The acetylperoxy radical (APR) has been found to be more reactive towards nitrogen monoxide than towards nitrogen dioxide. The bond strength of the O–O linkage in $CH_3C(=O)OONO$, however, is weaker than that of PAN or H_2O_2.

Peroxyacetyl nitrate (PAN) is a major class of eye irritant (lachrymators) in photochemical smog,[1–9] exhibiting toxicity in the inactivation of enzymes such as hemoglobin, papain, reduced ribonuclease and glutathione, and coenzyme A by the oxidation of the susceptible mercapto groups.[8,10,11] PAN has hitherto been considered to be formed in two distinct ways:

$$CH_3C{=}O \xrightarrow{O_2} CH_3C(=O)O_2 \xrightarrow{NO_2} CH_3C(=O)O_2NO_2$$

(Stephens's mechanism[2,6,8]) (1)

$$[CH_3C(=O)O_2NO] \xrightarrow{-NO_2} [CH_3C(=O)O] \xrightarrow{NO_3} CH_3C(=O)O_2NO_2$$

(Hanst's mechanism[4]) (2)

where the acetyl radical is produced by the photochemical decomposition of ketones or the oxidation of olefins and aldehydes in smog.[7] Louw *et al.*[6] and Cox *et al.*[12] recently supported Stephens's mechanism, but suggested the presence of a competitive reaction between $CH_3C(=O)O_2$ (APR) and NO.[12] Although there are some IR spectroscopic studies of PAN,[1,3,13] PAN has hitherto been the object of only limited investigation in terms of the molecular orbital treatment. The present MO study deals with the process of PAN formation.

Method of Calculation

Conformational optimizations were performed on $CH_3C{=}O$ $CH_3C(=O)O_2$, $CH_3C(=O)O_2NO$, and CH_3-$C(=O)O_2NO_2$ by means of the INDO method[14] which is reliable for bond angles but less so for bond lengths.[14,15] The optimization, by means of a repeated SCF-procedure for the minimization of the total energy of a molecule, was conducted by changing the geometric parameters in turn until the optimum conformations of identical bond length and angle (within ±0.01 Å and 1°) were reached, the parameters of which are shown in Fig. 1.

Results and Discussion

The σ-type acetyl radical undergoes a rapid reaction with O_2 in air to form the acetylperoxy radical (APR) *via* the overlapping between the singly-occupied (SO), sp²-like hybridized carbon orbital (spin density=0.62) on $CH_3C{=}O$ and the SO π_g-orbital of O_2 with a binding energy of 180.6 kcal/mol. APR

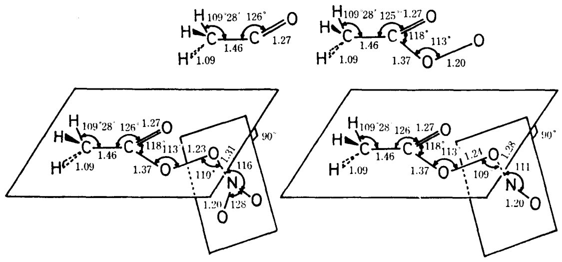
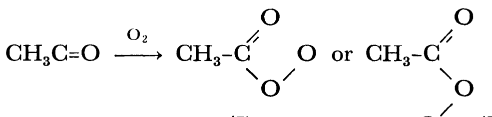


Fig. 1. Optimized geometric parameters for $CH_3C{=}O$, $CH_3C(=O)O_2$ $CH_3C(=O)O_2NO_2$, and $CH_3C(=O)O_2$-NO. (The HC–C(=O)–OO fragment is on the same plane.)



(I) (II) (3)

corresponds to I which is energetically more stable than II by 1.03 kcal/mol (rotational barrier around the C–O bond=4.86 kcal/mol). The SO orbital (located at −0.504 a.u.) on the terminal oxygen (spin density=0.819) in APR, which expands perpendicularly to the C(=O)–O–O plane, is capable of coupling with the nitrogen SO orbital (at −0.489 a.u.) on the NO_2 (spin density=0.383) or with that (at −0.454 a.u.) on the NO (spin density=0.468). The minimized energetic process of the above coupling reaction was followed by the optimization of the geometric parameters of $CH_3C(=O)O_2$–NO or $CH_3C(=O)O_2$–NO_2 along the O–N bond. As can be seen from Table 1, the APR–NO_2 reaction is more energetically favored than the APR–NO_2 reaction. The most stable $CH_3C(=O)O_2NO$ and $CH_3C(=O)$-O_2NO_2 are obtained at an O–N distance of 1.28 and 1.31 Å respectively. The nuclear-electron attraction (E_I) makes the APR–NO_2 reaction more favorable than the APR–NO reaction, but the increase in the internuclear and interelectron repulsions (E_N and E_{II} respectively) in the reaction is more remarkable in the APR–NO_2 reaction. That the APR–NO reaction predominates the APR–NO_2 reaction agrees with the priority of $CH_3C(=O)O_2NO$ formation in the following competitive reactions:

$$\text{APR} \xrightarrow[k]{NO} CH_3C(=O)O_2NO \qquad (4a)$$

$$(k/k' \simeq 1.7^{12)})$$

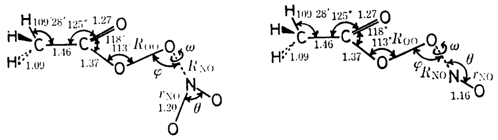
$$\text{APR} \xrightarrow[k']{NO_2} CH_3C(=O)O_2NO_2 \qquad (4b)$$

The relatively small amount of NO as compared with that of NO_2 in air ([NO]/[NO_2]=0.1(daytime)—1.0(night) in towns[12]), however, does not make Reaction 4a predominate over Reaction 4b in photochemical smog. The calculated binding energy of

Table 1. Changes in the geometric parameters and total energies (ΔE) along the reaction between APR and NO_2 and between APR and NO

R_{NO}/Å	∞	2.20	1.75	1.50	1.31	1.28
r_{OO}/Å	1.20 (1.20)	1.20 (1.21)	1.22 (1.22)	1.23 (1.23)	1.23 (1.24)	(1.24)
r_{NO}/Å	1.20 (1.16)	1.20 (1.16)	1.20 (1.16)	1.20 (1.16)	1.20 (1.16)	(1.20)
ϕ/deg.		100 (90)	102 (98)	105 (107)	110 (113)	(109)
ω/deg.[a]		0.0 (180)	0.0 (180)	0.0 (180)	0.0 (180)	(180)
θ/deg.	138.5	142 (92)	136 (100)	134 (109)	128 (115)	(111)
ΔE/a.u.[b]	0.0 (0.0)	0.135 (0.122)	−0.058 (−0.069)	−0.213 (−0.230)	−0.292 (−0.319)	(−0.324)

Values in parentheses are those for the APP-NO system. a) $\omega=0°$ in the following conformations. b) $\Delta E = E_{total}(\text{APR-NO}_2 \text{ or APR-NO}) - E_{total}(\text{APR}) - E_{total}(\text{NO}_2 \text{ or NO})$.



(HC-C(=O)-OO fragment is in the same plane).

the weakest O–O bond in $CH_3C(=O)OONO$ (249 kcal/mol) is less than that of the same bond in H_2O_2 (281 kcal/mol). Consequently, $CH_3C(=O)O_2NO$ undergoes thermal decomposition through the following reaction.

$$CH_3C(=O)O_2NO \xrightarrow{\Delta} CH_3C(=O)O + NO_2 \quad (5)$$

PAN formed by Reaction 4b has many rotational isomers (Fig. 2). The rotational barrier around the O–NO_2 bond was found to be 10.2 kcal/mol, around the O–O bond 1.66 kcal/mol, and around the C–O bond 11.9 kcal/mol. The bond strength of the O–O linkage (binding energy=273 kcal/mol) in PAN

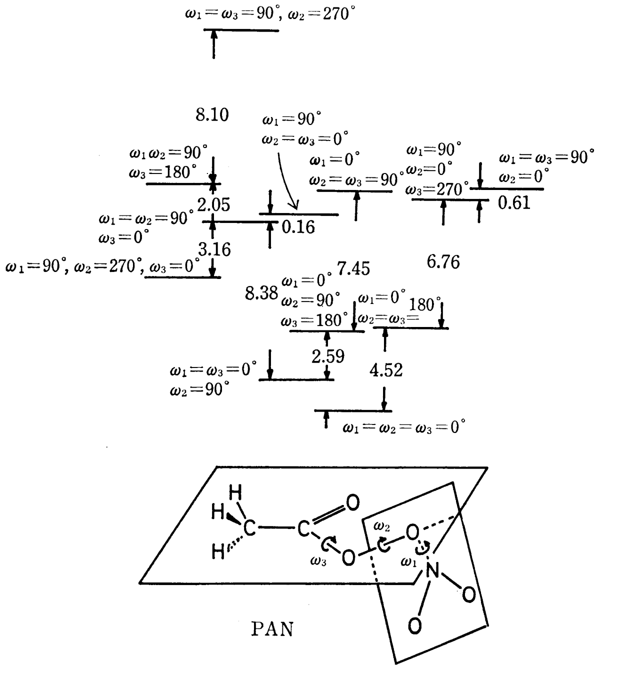


Fig. 2. Relative stability of the rotamers of PAN (energy difference: kcal/mol. $\omega_1=\omega_2=\omega_3=0$ and dihedral angle of the two planes=90° in the above energetically most stable conformation of PAN).

is of the same magnitude as that of H_2O_2, so that PAN is also thermally decomposed in the following way:[7]

$$\text{PAN} \xrightarrow{\Delta} [CH_3C(=O)O\text{-}\vdots\text{-}ONO_2] \longrightarrow$$

$$[CH_3\text{-}\vdots C(=O)O] + ONO_2 \longrightarrow CH_3ONO_2 + CO_2 \quad (6)$$

where the binding energy of the C–C bond in CH_3-C(=O)O has been calculated as 249 kcal/mol. The photo-irradiation of PAN in the daytime, however, may bring about [n→π*] type electron excitation on the carbonyl group (calculated excitation energy =227 kcal/mol). Such an electron excitation on the carbonyl group results in a weakening of the neighboring acyl bond in addition to that of the C=O bond *per se*; the excitation decreased the overlap population of the acyl bond by more than 10% with respect to the same bond in the ground state. Thus, the decomposition of PAN in the daytime may be expressed as follows:[7]

$$\text{PAN} \xrightarrow{h\nu} CH_3C{=}O + O_2NO_2 \xrightarrow{H_2O}$$
$$CH_3ONO_2 + CH_4 + CH_3OH + HCO_2H + NO_2 + O_2. \quad (7)$$

The radicals formed through the photochemical decomposition of PAN possibly abstract hydrogen from the SH group of the enzymes, thereby inactivating the enzymes *via* the formation of disulfides which are unobtainable from the *S*-acetyl group oxidation by PAN (or by H_2O_2).[11]

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