J. Phys. Chem. A **2002,** *106,* 3365−3370

Infrared Spectra and Density Functional Theory Calculations of Iminoxy Radicals Produced by Visible-Light-Induced Reaction between 1-Phenyl-1-Propyne and NO_2 in Low-Temperature Argon Matrixes[†]

Tomohiro Uechi, Satoshi Kudoh, Masao Takayanagi, and Munetaka Nakata*

Graduate School of BASE (Bio-Applications and Systems Engineering), Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan

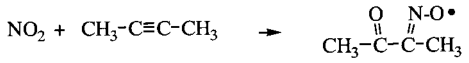
Received: May 4, 2001; In Final Form: July 12, 2001

Visible-light-induced reaction between 1-phenyl-1-propyne and NO_2 in low- temperature argon matrixes has been studied by Fourier transform infrared spectroscopy with an aid of density functional theory (DFT) calculation. Infrared bands observed upon 580-nm irradiation are assigned to acetyl phenyl iminoxy radical, which is produced by recombination of acetylphenylmethylene, a ketocarbene intermediate, with a reactive coproduct, NO. Conformations around the OC−CN and C═N axes of acetyl phenyl iminoxy radical are determined by a comparison of the observed and calculated wavenumbers. A small amount of methylphenylketene is produced from ketocarbene by migration of the methyl group. The branching ratio of the migration against the recombination is estimated to be 0.072 ± 0.006 by an analysis of absorption-growth behavior for the infrared bands of methylphenylketene and acetyl phenyl iminoxy radical.

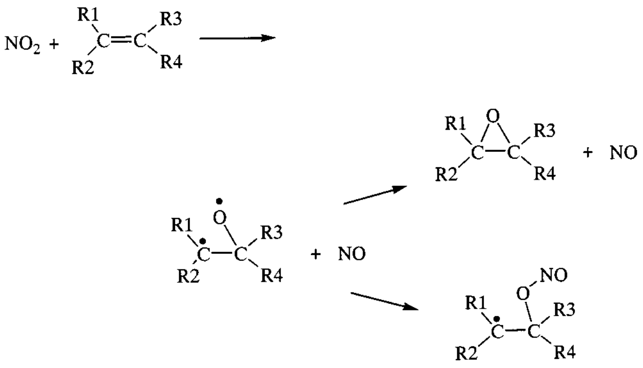
Introduction

Iminoxy radicals, which contain C═N−O• group, are widely used in studies of electron paramagnetic resonance (EPR) as spin probes. Structures of the hyperfine splitting constants have been studied experimentally[1−4] and theoretically[5] to determine whether these radicals are σ- or π-type. However, fewer papers have been published to determine geometrical structures of iminoxy radicals by analyzing vibrational spectra. Infrared spectra of the simplest iminoxy radical, $CH_2{=}N{-}O\bullet$, produced from ketene and NO upon 380- and 355-nm laser irradiation were measured by McCluskey and Frei.[6] Infrared spectra were observed for acetyl methyl iminoxy radical (3-oxobutan-2-iminoxyl) produced by visible-light-induced reaction between NO_2 and 2-butyne in low-temperature argon matrices (Scheme 1).[7] The geometrical structures containing conformations around the OC−CN and C═N bond axes were determined by a vibrational analysis with an aid of density functional theory (DFT) calculation.[8] A similar experiment was performed for the visible-light-induced reaction between propyne and NO_2, and infrared spectra of formyl methyl iminoxy radical were observed by Harrison and Frei.[9,10] No other infrared bands of iminoxy radicals seem to have been published.

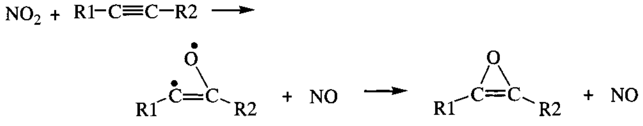
SCHEME 1



SCHEME 2



SCHEME 3



In visible-light-induced bimolecular reactions between NO_2 and various organic compounds in low-temperature argon matrixes,[7−26] transfer of the oxygen atom of NO_2 excited electronically by visible radiation occurs first. In the case of alkene such as ethene, propene, and butene, the first reaction intermediate is oxirane biradical, which changes to oxirane by ring closure or to nitrite radical by recombination with a reactive coproduct, NO (Scheme 2). More interesting results are obtained when an alkyne such as ethyne, propyne, and 2-butyne is chosen as a reaction partner of NO_2 because the transfer of oxygen atom produces oxirene biradical as the first reaction intermediate. This biradical could be transformed to oxirene if ring-closure occurs (Scheme 3). The stability of oxirene has been discussed experimentally and theoretically for a long time. Schaefer and his group[27−29] performed optimization by using various basis sets and showed that oxirene was stable in the triple-ζ level, although the barrier height for conversion to ketene was small. It had been reported earlier by Bachmann et al. that dimethyloxirene was trapped in a cryogenic matrix by photochemically induced Wolff rearrangement of 3-diazo-2-butanone.[30] However, their assignment is questionable because the observed band was nearly equal to that of dimethylketene.[7] Strausz et al. tried to trap bis(trifluoromethyl)oxirene, which seemed to be more stable

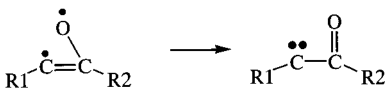
---

[†] Part of the special issue "Mitsuo Tasumi Festschrift".

* To whom correspondence should be addressed. E-mail: necom@cc.tuat.ac.jp. Tel: +81-42-388-7349. Fax: +81-42-388-7349.

10.1021/jp011689c CCC: $22.00

SCHEME 4



than dimethyloxirene, by photolysis of perfluoro-3-diazo-2-butanone in a cryogenic matrix and reported that they could identify the corresponding oxirene.[31−33] According to Singmaster et al.,[34] however, similar infrared bands were observed on the photoreaction between ozone and hexafluoro-2-butyne; they assigned the bands to ketocarbene produced from oxirene biradical instead of oxirene by electron rearrangement (Scheme 4). Our previous study of the bimolecular reaction between NO_2 and 2-butyne supports the production of ketocarbene, which changes to iminoxy radical by recombination with NO.[7]

In the present work, visible-light-induced reaction between 1-phenyl-1-propyne and NO_2 in low-temperature argon matrixes has been studied. Phenyl-group substitution may stabilize ketocarbene because of π-electron conjugation. DFT (density functional theory) calculations[35−37] are used to propose a production mechanism of iminoxy radical through oxirene biradical, oxirene, and ketocarbene as reaction intermediates.

Experimental and Calculation

Matrix-Isolation Infrared Spectroscopy. The sample of 1-phenyl-1-propyne was purchased from Tokyo Chemical Industry Co., Ltd. and was used after trap-to-trap vacuum distillation at 77 K. NO_2 was purchased from Sumitomo Seika and was used after freeze-pump cycles at 77 and 193 K. The sample vapors were premixed separately with argon gas (Takachiho, 99.9999% purity) in glass bulbs. The premixed gases were co-deposited in a vacuum chamber on a CsI plate at 20 K cooled by a closed-cycle helium refrigeration unit. The mixing ratio used was 1-phenyl-1-propyne/NO_2/Ar = 1/1/180. The sample of $^{15}NO_2$ (99.8 atom % ^{15}N) was purchased from Shoko Co. Ltd. and was used without purification. An argon ion laser-pumped CW dye laser was used to induce bimolecular reaction. Rhodamine 6G was used in the range of 570−630 nm. The laser beam was defocused with a lens to a diameter of 10 mm on the matrix sample. The laser power was typically 200 mW cm^{-2}. Infrared spectra were recorded with 0.5 cm^{-1} resolution with a JASCO 8000S Fourier transform infrared spectrophotometer. Other experimental details have been reported elsewhere.[23]

DFT Calculations. The calculations were performed using the GAUSSIAN 98 program[38] with the 6-31+G* basis set, where the hybrid density functional[39] in combination with the Lee, Yang, and Parr correlation functional[40] and the gradient-corrected functional of Becke[41] were used. In addition, open-shell wave functions were employed with the local spin density exchange functional of Slater[42] (UB3LYP) for the calculation of the doublet state for iminoxy radicals and the triplet states for oxirene and ketocarbenes.

Results and Discussion

Infrared Spectra of Photoproducts. The spectra of 1-phenyl-1-propyne and NO_2 in low-temperature argon matrixes were measured by a standard technique. After the measurement, the matrix sample was exposed to dye-laser light. Photoreaction between 1-phenyl-1-propyne and NO_2 occurred below 610 nm. A difference spectrum between those measured before and after 580-nm irradiation is shown in Figure 1. Most of the decreasing bands, marked with a circle, are assigned to 1-phenyl-1-propyne; their peak values are consistent with those reported in gas phase[43] within 4 cm^{-1}, while the 1620 cm^{-1} band is assigned to the stretching mode of NO_2. Additional bands, marked with a cross, assignable to trace impurities, N_2O_3 and N_2O_4, were also observed.[14,15] The band appearing at 2112 cm^{-1} is assigned to a photoproduct, ketene, as described below. The weak band appearing at 1872 cm^{-1} can be assigned to NO, which is a reaction coproduct of ketene, by a comparison with the results of our previous studies.[7] The observed wavenumbers and relative intensities of the other increasing bands are summarized in Table 1.

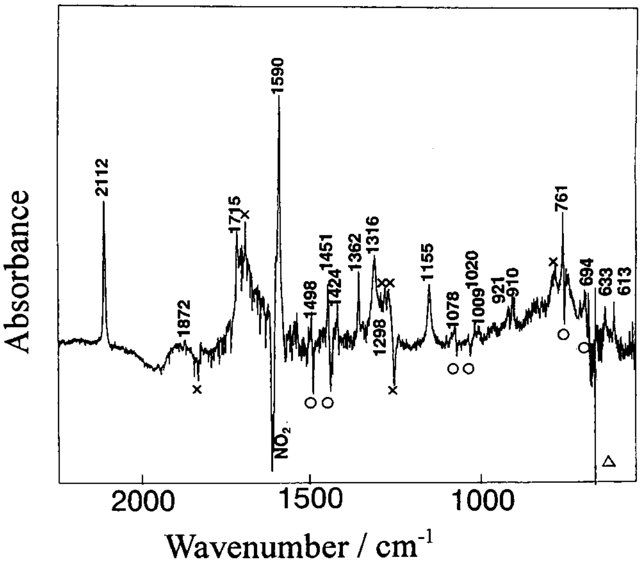


Figure 1. A difference infrared spectrum obtained upon 580-nm irradiation (200 mW cm^{-2}) of a matrix, 1-phenyl-1-propyne/$^{14}NO_2$/Ar = 1/1/180, for 120 min. O, X, and △ represent bands assigned to 1-phenyl-1-propyne, NO_x, and CO_2 in atmosphere, respectively.

A similar experiment using $^{15}NO_2$ was performed. The difference spectrum is shown in Figure 2. The weak ^{15}NO band is observed at 1839 cm^{-1}, which is consistent with the reported value.[7] Most of the increasing bands are observed at wavenumbers equal to those for the normal species, except that the 1590 cm^{-1} band of the normal species is shifted to 1565 cm^{-1} for the ^{15}N-isotope species.

Identification of Photoproducts. The intense band appearing at 2112 cm^{-1} shows no ^{15}N-isotope shift. A similar band, observed in the spectra of a photoproduct between 2-butyne and NO_2, was assigned to the C=C=O stretching mode of dimethylketene produced from acetylmethylmethylene, dimethylketocarbene, by migration of methyl group.[7] Therefore, it is highly likely that the 2112 cm^{-1} band is due to methylphenylketene. The absence of the ^{15}N-isotope shift in this band supports our assignment. No other bands of methylphenylketene are found in the spectra, probably because of their small intensity. It is well known that the intensity of the C=C=O stretching mode of ketene derivatives is exceptionally high. McMahon and Chapman[44] observed infrared spectra of methylphenylketene in low-temperature matrixes and reported only one band of the C=C=O stretching mode appearing at 2110 cm^{-1}. The intensity ratio of NO and ketene derived from calculation, estimated to be 0.043, is consistent with the observed value, 0.05 ± 0.01.

Since the 1590 cm^{-1} band shows a ^{15}N-isotope shift of 25 cm^{-1}, it is assigned to the C=N stretching mode. On the other hand, the band with medium intensity appearing at 1715 cm^{-1} must be assigned to a C=O stretching mode. These bands are similar to those for acetyl methyl iminoxy radical, where the

TABLE 1: Observed and Calculated Wavenumbers (cm^{-1}) and Relative Intensities

			calc.					
obs.			AP-TT[a]			BM-TT[b]		
ν			int.[c]			ν[d]		
normal	^{15}N	int.[c]	normal	^{15}N	int.[e]	normal	^{15}N	int.[e]
1715[f]	1713	m	1700[f]	1697	66	1659[f]	1652	64
1590[g]	1564	s	1599[g]	1566	368	1596[g]	1573	412
			1579	1583	32	1582	1582	26
			1560	1560	1	1561	1560	25
1498	1498	w	1477	1475	11	1472	1472	2
1451	1451	w	1437	1437	12	1447	1446	8
1424	1424	w	1428	1428	25	1439	1438	6
			1427	1426	3	1427	1426	9
1362	1362	m	1355	1355	25	1357	1357	13
			1321	1321	8	1327[h]	1324	38
1316[h]	1311	m	1305[h]	1301	56	1311	1311	4
1298[i]	1297	m	1284	1282	47	1292	1291	18
			1244	1243	86	1272	1271	158
			1177	1177	2	1165	1166	2
			1147	1147	<1	1147	1147	47
1155	1154	m	1130	1129	42	1145	1145	18
1078	1078	w	1074	1074	10	1069	1069	5
1020	1020	w	1019	1019	2	1014	1014	2
1009	1009	w	1005	1006	3	1009	1009	<1
			986	986	6	985	983	47
			974	974	<1	975	975	3
			966	966	<1	970	969	<1
			946	945	<1	949	949	1
921	921	w	901	901	4	911	911	2
910	910	w	885	884	43	880	879	27
			817	817	<1	827	826	3
761	761	m	744	744	39	771	771	7
		w	695	692	8	709	705	5
694	694	m	670	670	41	689	689	78
633	633	w	612	611	2	669	669	9
			605	605	3	634[j]	629	37
613[j]	609	m	596[j]	592	46	605	605	<1

[a] Trans-trans acetyl phenyl iminoxy radical. [b] Trans-trans benzoyl methyl iminoxy radical. [c] Relative intensities. s, m, and w represent strong, medium, and weak, respectively. [d] Wavenumbers calculated by DFT/UB3LYP/6-31+G*. A scaling factor of 0.96 is used. [e] Relative intensities of normal species calculated by DFT/UB3LYP/6-31+G*. [f] C=O stretching mode. [g] C=N stretching mode. [h] Related to N−O stretching mode. [i] Disturbed by NO_x bands. [j] Related to C=N−O bending mode.

corresponding bands for the most stable conformer were observed at 1591 and 1711 cm^{-1}, respectively.[7] In summary, the infrared bands of the final product are assigned to one of the iminoxy radical derivatives with methylphenylketene.

Conformation of Iminoxy Radical. *Calculated Relative Energies.* Two kinds of iminoxy radicals are possible for products of the reaction between 1-phenyl-1-propyne and NO_2; one is acetyl phenyl iminoxy radical and the other is benzoyl methyl iminoxy radical. Furthermore, both trans and cis conformations around the OC−CN and C=N axes are possible as well as acetyl methyl iminoxy radical.[7] Then, eight conformers shown in Figure 3 are candidates for the final product, where AP and BM denote acetyl phenyl and benzoyl methyl iminoxy radicals, respectively. The first and second symbols, T or C, represent trans or cis conformations around the OC−CN and C=N axes, respectively, as defined in the figure. Among these conformers, AP-CT, AP-CC, BM-CT, and BM-CC seem to be less stable than the other conformers because one of the hydrogen atoms in the phenyl group conflicts with that of the methyl group. Likewise, one of the hydrogen atoms in the phenyl group of BM-TC conflicts with the oxygen atom of the iminoxy group.

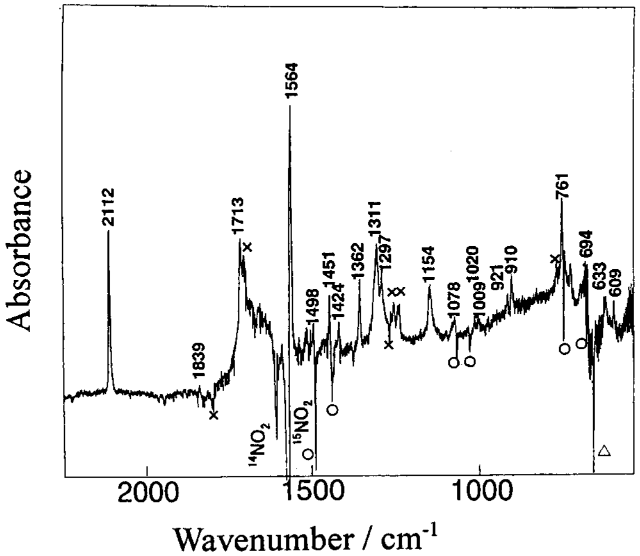


Figure 2. A difference infrared spectrum obtained upon 580-nm irradiation (200 mW cm^{-2}) of a matrix, 1-phenyl-1-propyne/$^{15}NO_2$/Ar = 1/1/180, for 120 min. O, X, and △ represent bands assigned to 1-phenyl-1-propyne, NO_x, and CO_2 in atmosphere, respectively.

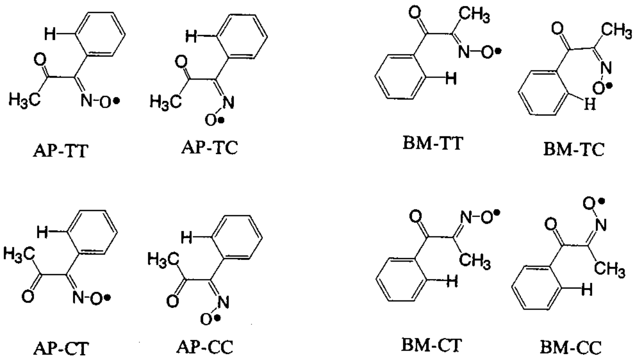


Figure 3. Four possible conformers of acetyl phenyl iminoxy radical (AP) and benzoyl methyl iminoxy radical (BM). The first and second symbols, T or C, denote conformations of O and N around the OC−CN axis and of CO and O• around the C=N axis, trans or cis, respectively.

To confirm the above speculation on the conformational stability, a DFT calculation was performed. The spin contamination due to the use of unrestricted open-shell methodology was found to be very low, where the value of $S(S + 1)$ was essentially equal to 0.75 within 0.01. This finding leads to the conclusion that the DFT calculations represent the doublet state with negligible contamination from the other multiplet states.

The optimized geometries obtained are planar for all the conformers; their geometrical parameters of the molecular skeleton and relative energies are summarized in Table 2. The OC−CN and NC−CH_3 bond distances in BM-CC and BM-CT are longer than those in BM-TT, probably because of the interaction between the phenyl and methyl groups, as described above. An analogous tendency is found in the C−CN−CH_3 bond angle; those in BM-CC and BM-CT are about 5° larger than that in BM-TT. The C=N−O• bond angle in BM-TC is about 4° larger than that in BM-TT, while the C−CN−CH_3 bond angle in BM-TC is 3° smaller than that in BM-TT, probably because of the interaction between the phenyl and iminoxy groups.

Since the relative energies of AP-CT, AP-CC, BM-CT, BM-CC, and BM-TC are 10 kJ mol^{-1} higher than that of the most stable conformer, BM-TT, the candidates for the iminoxy radical

TABLE 2: Optimized Geometry (in Å or Degrees) and Relative Energies (in kJ mol^{-1}) of Conformers of Acetyl Phenyl (AP) and Benzoyl Methyl (BM) Iminoxy Radicals[a]

conformer	AP-TT	AP-TC	APCC	APCT	BM-TT	BM-TC	BM-CC	BM-CT
ΔE[b]	3.43	9.34	13.03	22.17	0.00	11.01	17.52	18.73
r(N−O•)	1.226	1.226	1.223	1.220	1.227	1.230	1.224	1.225
r(C═N)	1.303	1.301	1.305	1.302	1.296	1.293	1.302	1.297
r(OC−CN)	1.504	1.514	1.504	1.505	1.492	1.513	1.502	1.501
r(C═O)	1.221	1.220	1.221	1.221	1.229	1.225	1.225	1.225
r(NC−R)[c]	1.485	1.485	1.486	1.489	1.506	1.506	1.509	1.512
r(OC−R)[c]	1.519	1.513	1.519	1.517	1.497	1.491	1.501	1.497
(C═N−O•)	135.4	136.5	131.1	134.5	132.6	136.5	131.8	132.2
<(OC−C═N)	113.0	120.3	116.7	113.8	118.1	122.7	116.4	114.7
<(O═C−CN)	121.0	119.1	120.0	120.5	118.2	116.9	119.8	120.2
<(C−CN−R)[c]	124.9	122.9	125.5	125.2	121.3	118.3	126.2	126.0
<(R−CO−C)[c]	117.8	119.1	118.6	118.1	121.0	121.5	120.1	119.1

[a] Other structural parameters are available upon request. [b] Relative energies. [c] R represents CH_3 or C_6H_5.

produced in low-temperature matrixes are the remaining conformers, AP-TC, AP-TT, and BM-TT.

In our previous study of acetyl methyl iminoxy radical,[7] it was concluded that the TC conformer was easily isomerized to the TT conformer upon visible-light irradiation, resulting in the absence of the observed infrared bands for the TC conformer. On this basis, AP-TC is removed from the candidates. Although visible absorption spectra of the radicals may be useful to explain the absence of TC, it was difficult to measure them because the amount of TC was too small, the lifetime was too short, and the spectrum was disturbed by No_x bands. Our assumption of excluding TC is further supported by the reports of Alberti et al.;[45] they studied conformations of some iminoxy radicals in solution by electron spin resonance spectroscopy and concluded that the anti conformation around the C═N axis of phenyl iminoxy radical was more stable than the syn. In other words, the benzene ring and the oxygen atom are placed on the same side of the C═N bond. Thus, we assign the observed bands for iminoxy radical to AP-TT or BM-TT.

Calculated Vibrational Wavenumbers. A series of our conformational studies have shown that most of the vibrational wavenumbers predicted by density functional theory are consistent with the corresponding observed bands within 10 cm^{-1} if a suitable scaling factor is used.[46−53] Thus, accurate predictions by DFT have enabled correct identification of conformers among various possibilities no matter whether their spectral patterns are clearly distinguishable from one another. To identify the present iminoxy radical, the observed vibrational wavenumbers are compared with the calculated values for AP-TT and BM-TT obtained by DFT in Table 1, where a scaling factor of 0.96 is used.[54,55] The observed wavenumber for C═N stretching, 1590 cm^{-1}, is consistent with the calculated values for both AP-TT, 1599 cm^{-1}, and BM-TT, 1596 cm^{-1}, within 10 cm^{-1}. The corresponding observed wavenumber for the ^{15}N species, 1564 cm^{-1}, is also consistent with the calculated values, 1566 cm^{-1} (AP-TT) and 1573 cm^{-1} (BM-TT). On the other hand, the predicted wavenumbers of the C═O stretching band for AP-TT is 43 cm^{-1} higher than that of BM-TT. The wavenumbers of C═O stretching bands of acetyl compounds, 1725−1705 cm^{-1}, are known to be generally higher than those of benzoyl compounds, 1690−1680 cm^{-1}.[56] The observed wavenumbers for C═O stretching, 1715 cm^{-1}, is consistent with that for the acetyl compounds. An intense band for BM-TT is predicted at 1273 cm^{-1}, but no intense band of the iminoxy radical is found around this wavenumber although this region is slightly disturbed by NO_x bands. Hence, we assign our observed infrared bands to AP-TT. The 1316 and 613 cm^{-1} bands are found to be due to N−O stretching and C═N−O bending modes of AP-TT, respectively, where the observed ^{15}N isotope shifts, ca. 5 cm^{-1}, are consistent with the corresponding calculated values.

Reaction Mechanism. One may have a question why the infrared bands of the less stable conformer, AP-TT, instead of the more stable conformer, BM-TT, are observed. To understand this selectivity, we performed a similar DFT calculation for the singlet and triplet states of reaction intermediates, oxirene and two kinds of ketocarbenes, acetylphenylmethylene and benzoylmethylmethylene. The energies of ketocarbenes in the lowest triplet state are calculated to be about 10 kJ mol^{-1} higher than the corresponding values in the singlet state, while that of oxirene is 134 kJ mol^{-1} above the singlet state. So, we discuss the reaction between NO_2 and 1-phenyl-1-propyne on the singlet potential surface, which is shown in Figure 4.

The first reaction step is the oxygen atom transfer from electronically excited NO_2 to 1-phenyl-1-propyne to produce 1-methyl-2-phenyl oxirene biradical and 2-methyl-1-phenyl oxirene biradical. We tried to optimize the geometry of oxirene biradicals, but one of the calculated vibrational wavenumbers was imaginary. Thus, we assume that the oxirene biradicals are on saddle points of the potential surface and immediately change to oxirene by ring closure or to ketocarbenes by rearrangement of electrons. The results of our calculation show that the relative energies of both oxirene and benzoylmethylmethylene are about 30 kJ mol^{-1} higher than that of acetylphenylmethylene. This result suggests that the nonbonded electron pair on the carbon between the phenyl and carbonyl groups is more stabilized by π-electrons conjugation than that between the methyl and carbonyl groups. Since the energy differences between oxirene biradicals and oxirene are estimated to be about 0.2 kJ mol^{-1}, it is possible that benzoylmethylmethylene is immediately isomerized to acetylphenylmethylene through oxirene and oxirene biradicals, and acetyl phenyl iminoxy radical, AP-TT, is produced from acetylphenylmethylene by recombination with a reactive coproduct, NO. A similar discernment is given by Frei to explain the reaction mechanism between propyne and NO_2, where infrared bands of formyl methyl iminoxy radical were observed but not of acetyl iminoxy radical.[9,10]

Another reason for the selectivity may be steric hindrance in the reactant, 1-phenyl-1-propyne. Oxygen-atom transfer is likely to occur more easily at the smaller methyl group than at the larger phenyl group. In our previous study of the reaction between NO_2 and propene, infrared bands of only a secondary propyl nitrite radical were observed as an intermediate.[13] This finding also supports the preferred approach of the oxygen atom to the less hindered side.

Branching Ratio. Methylphenylketene is produced from acetylphenylmethylene by migration of the methyl group. This

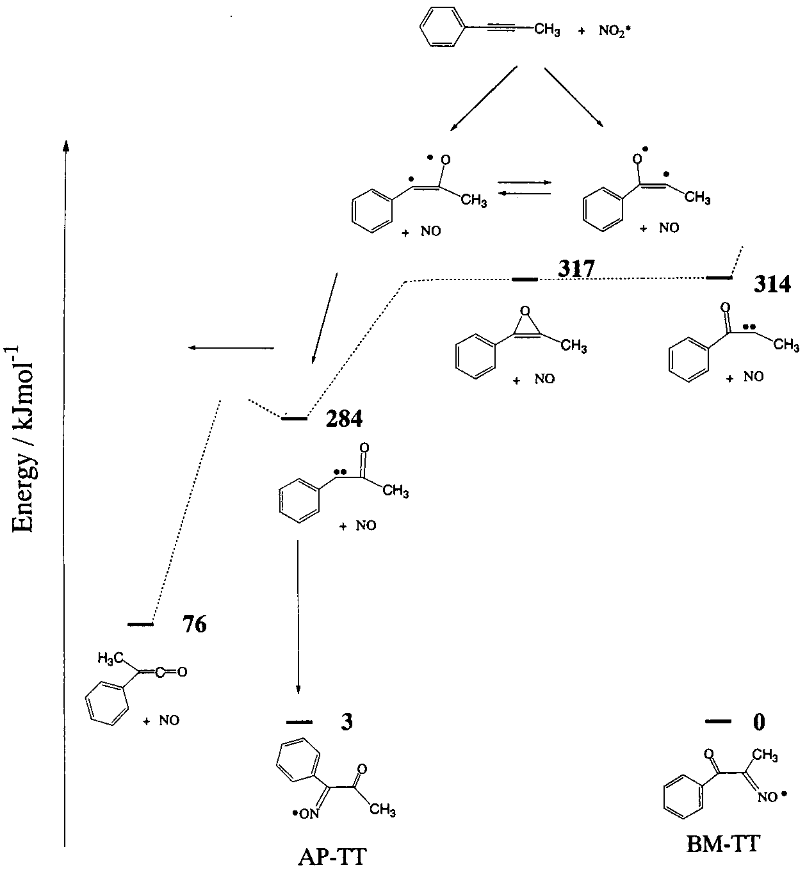


Figure 4. A schematic energy-level diagram of singlet state for the 1-phenyl-1-propyne and NO_2 system obtained by DFT/B3LYP/6-31+G*.

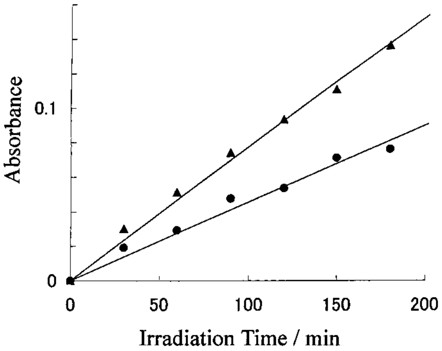


Figure 5. Absorbance-growth behavior of infrared bands. Closed triangles and circles represent the bands of methylphenylketene (2112 cm^{-1}) and acetyl phenyl iminoxy radical (1155 cm^{-1}), respectively. Solid lines represent the calculated values obtained by a least-squares fitting.

reaction is not the main path because the amounts of ketene and a coproduct, NO, are small, although the infrared band intensity of the C=C=O stretching mode is almost equal to that of the C=N stretching mode of iminoxy radical. To determine the branching ratio between methyl-group migration to produce ketene and recombination with NO to produce iminoxy radical, we examined the absorbance-growth behavior of the 2112 cm^{-1} band for ketene and the 1155 cm^{-1} band for AP-TT. The dependence of the absorbance on irradiation time is illustrated in Figure 5. When the first-order reaction is assumed, the absorbance can be represented by resolving the rate equations as

$$A^{K} = A^{R}(\epsilon^{K}/\epsilon^{R})[k^{K}/(k^{K} + k^{I})][1 - \exp(-(k^{K} + k^{I})t] \quad (1)$$

$$A^{I} = A^{R}(\epsilon^{I}/\epsilon^{R})[k^{I}/(k^{K} + k^{I})][1 - \exp(-(k^{K} + k^{I})t] \quad (2)$$

where A^R, A^K, and A^I represent the absorbance for the reactant and the final products, ketene and iminoxy radical. Symbols ϵ^R, ϵ^K, ϵ^I represent extinction coefficients for the corresponding species. The branching ratio for k^K and k^I is derived from these equations as

$$k^{K}/k^{I} = (A^{K}/A^{I})(\epsilon^{I}/\epsilon^{K}) \quad (3)$$

The ratio of the extinction coefficients, ϵ^I/ϵ^K, is estimated by a DFT calculation to be 0.043. The average value of the ratio for the absorbance, A^K/A^I, is determined experimentally to be 1.66 ± 0.14 at the 580-nm irradiation. Then, the branching ratio, k^K/k^I, is calculated to be 0.072 ± 0.006. This means that the yield of methylphenylketene is less than 8%. Dependence of the branching ratio on wavelength is also examined. However, it is essentially unchanged in the range between 605 and 575 nm. By assuming that the ratio of A^K and A^I is a constant, 1.66, the sum of k^K and k^I is determined by a least-squares fitting. The obtained value is 0.000234 ± 0.000024 min^{-1}. The observed values are consistent with the calculated values represented by solid lines within experimental error, as shown in Figure 5.

Conclusion

Visible-light-induced reaction between 1-phenyl-1-propyne and NO_2 in low-temperature argon matrixes is studied by infrared spectroscopy and density functional theory calculation. The final reaction products are identified as methylphenylketene and acetyl phenyl iminoxy radical by a comparison of the observed and calculated wavenumbers, where the conformations of O and N around the OC−CN axis and of CO and O• around the C=N axis are also determined to be trans. The stereoselectivity is explained in terms of the stability of the reaction intermediate, ketocarbene, and the interaction between one of the hydrogen atoms in the phenyl ring and the methyl group or N−O•. The branching ratio of the two products, methylphenylketene/acetyl phenyl iminoxy radical, is estimated from the absorbance-growth behavior to be 0.072 ± 0.006.

Acknowledgment. The authors thank Professor Kozo Kuchitsu (Josai University) for his helpful discussions.

References and Notes

(1) Norman, R. O. C.; Gilbert, B. C. *J. Phys. Chem.* **1966**, *71*, 14.
(2) Gilbert, B. C.; Gulick, W. M., Jr. *J. Phys. Chem.* **1969**, *73*, 2449.
(3) Gilbert, B. C.; Malatesta, V.; Norman, R. O. C. *J. Am. Chem. Soc.* **1971**, *93*, 3290.
(4) Brkenshire, J. L.; Roberts, J. R.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 7040.
(5) Jaszewski, A. R.; Jezierska, J.; Jezierski, A. *Chem. Phys. Lett.* **2000**, *319*, 611.
(6) McCluskey, M.; Frei, H. *J. Phys. Chem.* **1993**, *97*, 5204.
(7) Nakata, M.; Frei, H. *J. Am. Chem. Soc.* **1992**, *114*, 1363.
(8) Kudoh, S.; Uechi, T.; Takayanagi, M.; Nakata, M.; Frei, H. *Chem. Phys. Lett.* **2000**, *283*, 328.
(9) Harrison, J. A.; Frei, H. *J. Phys. Chem.* **1994**, *98*, 12142.
(10) Harrison, J. A.; Frei, H. *J. Phys. Chem.* **1994**, *98*, 12152.
(11) Nakata, M.; Shibuya, K.; Frei, H. *J. Phys. Chem.* **1990**, *94*, 8168.
(12) Fitzmaurice, D. J.; Frei, H. *J. Phys. Chem.* **1992**, *96*, 10308.
(13) Nakata, M.; Somura, Y.; Takayanagi, M.; Tanaka, N.; Shibuya, K.; Uchimaru, T.; Tanabe, K. *J. Phys. Chem.* **1996**, *100*, 15815.
(14) Nakata, M.; Frei, H. *J. Am. Chem. Soc.* **1989**, *111*, 5240.
(15) Nakata, M.; Frei, H. *J. Phys. Chem.* **1989**, *93*, 7670.
(16) Nakata, M.; Frei, H. *J. Chem. Soc. Jpn.* **1989**, 1412.
(17) Fitzmaurice, D. J.; Frei, H. *Chem. Phys. Lett.* **1992**, *192*, 166.
(18) Nakata, M. *Spectrochim. Acta* **1994**, *50A*, 1455.
(19) Blatter, F.; Frei, H. *J. Phys. Chem.* **1993**, *97*, 3266.
(20) Fitzmaurice, D. J.; Frei, H. *J. Phys. Chem.* **1991**, *95*, 2652.
(21) Tanaka, N.; Kajii, Y.; Shibuya, K.; Nakata, M. *J. Phys. Chem.* **1993**, *97*, 7048.
(22) Tanaka, N.; Nakata, M.; Shibuya, K. *J. Photochem. Photobiol*. **1997**, *106*, 113.
(23) Tanaka, N.; Oike, J.; Y. Kajii, Shibuya, K.; Nakata, M. *Chem. Phys. Lett*. **1993**, *97*, 70.
(24) Tanaka, N.; Oike, J.; Shibuya, K.; Nakata, M. *J. Phys. Chem.* **1996**, *100*, 4873.
(25) Tanaka, N.; Oike, J.; Shibuya, K.; Nakata, M. *Res. Chem. Intermed.* **1998**, *8*, 893.
(26) Kudoh, S.; Uechi, T.; Takayanagi, M.; Nakata, M.; Tanaka, N.; Shibuya, K. *J. Mol. Struct.* **2000**, *524*, 251.
(27) Vacek, G.; Galbraith, J. M.; Yamaguchi, Y.; Schafer, H. F.; Nobes, R. H.; Scott, A. P.; Radom, L. *J. Phys. Chem*. **1994**, *98*, 8660.
(28) Fowler, J. E.; Galbraith, J. M.; Vacek, G.; A. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1994**, *116*, 9311.
(29) Scott, A. P.; Nobes, R. H.; Schaefer, H. F. *J. Am. Chem. Soc.* **1994**, *116*, 10159.
(30) Bachmann, C.; N'Guessan, T. Y.; Debu, F.; Monnier, M.; Pourcin, J.; Aycard, J. P. C. R.; Bodot, H. *J. Am. Chem. Soc.* **1990**, *112*, 7488.
(31) Torres, M.; Bourdelande, J. L.; Clement, A.; Strausz, O. P. *J. Am. Chem. Soc.* **1983**, *105*, 1698.
(32) Laganis, E. D.; Janik, D. S.; Curphey, T. J.; Lemal. *J. Am. Chem. Soc.* **1983**, *105*, 7457.
(33) Mahaffy, P. G.; Visser, D.; Torres, M.; Bourdelande, J. L.; Clement, A.; Strausz, O. P. *J. Org. Chem.* **1987**, *52*, 2680.
(34) Singmaster, K. A.; Jonnalagadda, S.; Chan, S. *J. Am. Chem. Soc.* **2000**, *122*, 9078.
(35) Ziegler, T. *Can. J. Chem.* **1995**, *73*, 743.
(36) Labanowski, J.; Andzelm, J. W. *Density Functional Methods in Chemistry*; Springer-Verlag: New York, 1991.
(37) Seminario, J. M.; Politzer, P. *Modern Density Functional Theory: A Tool for Chemistry*; Elsevier: Amsterdam, 1995.
(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.
(39) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(40) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(41) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(42) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4.
(43) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*; Aldrich Chemical Company, Inc.: Milwaukee, Wisconsin, 1989; Vol. 3.
(44) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683.
(45) Alberti, A.; Barbaro, G.; Battaglia, A.; Guerra, M. *J. Org. Chem.* **1981**, *46*, 742.
(46) Kudoh, S.; Takayanagi, M.; Nakata, M. *Chem. Phys. Lett.* **2000**, *322*, 363.
(47) Kudoh, S.; Takayanagi, M.; Nakata, M. *J. Photochem. Photobiol., A* **1999**, *123*, 25.
(48) Kudoh, S.; Takayanagi, M.; Nakata, M. *Chem. Phys. Lett.* **1999**, *308*, 403.
(49) Kudoh, S. Takayanagi, M. Nakata, M. *J. Mol. Struct*. **1999**, *475*, 253.
(50) Kudoh, S.; Onoda, K.; Takayanagi, M.; Nakata, M. *J. Mol. Struct.* **2000**, *524*, 61.
(51) Kudoh, S.; Takayanagi, M.; Nakata, M. *J. Mol. Struct.* **1997**, *413*/*414*, 365.
(52) Kudoh, S.; Takayanagi, M.; Nakata, M.; Ishibashi, T.; Tasumi, M. *J. Mol. Struct.* **1999**, *479*, 41.
(53) Kudoh, S.; Takayanagi, M.; Nakata, M. *Fourier Transform Spectrosc.* **2000**, 349.
(54) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
(55) Zhou, X.; Wheeless, C. J. M.; Liu, R. *Vib. Spectrosc.* **1996**, *12*, 53.
(56) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975; Vol. 1.