Visible Light Induced Reactions of NO₂ with Conjugated Dienes in a Low-Temperature Ar Matrix

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Visible light induced oxygen atom transfer from NO₂ to conjugated dienes has been investigated in a lowtemperature Ar matrix, where the dienes are 1,3-butadiene (BD), 2-methyl-1,3-butadiene (isoprene), and 2,3dimethyl-1,3-butadiene (DMB). In each diene/NO₂/Ar system, the corresponding nitrite radical, oxirane, aldehyde, and NO were obtained as the photochemical reaction products. The reactions are initiated by the formation of undetectable short-lived oxirane biradical and NO due to visible light induced O atom transfer from NO₂ to the conjugated dienes. (1) The recombination of oxirane biradicals and neighboring NO gives the nitrite radicals as the photochemical intermediate. (2) The ring closure of the biradicals leads to the formation of oxiranes. (3) The intramolecular H atom transfer of biradicals leads to the formation of aldehydes. The visible photolysis of the nitrite radicals gives rise to oxirane, aldehyde, and NO. The reaction rates are derived by measuring the absorbance changes of the products upon the 582-nm irradiation. The methyl substituent effect on the reactivity is discussed.

Introduction

Recent photochemical studies¹⁻⁹ on the NO₂ reactions with alkenes in low-temperature matrices revealed a mechanism involving oxygen atom transfer from photoexcited NO₂ to alkenes to produce oxiranes, aldehydes, and nitrite radicals. The nitrite radicals are able to absorb visible light and to decompose further into oxirane, aldehyde, and NO. The O atom transfer reactions are specified by the photoexcitation of NO₂ with visible light (red-to-yellow) longer than the dissociation threshold wavelength ($\lambda = 398$ nm). Alkenes do not absorb the visible light, and the occurrence of bimolecular reactions between photoexcited NO₂ and alkenes would be evident. This mild photo-oxidation method of alkenes using NO₂ is expected to be used in a variety of photochemical systems.

In the present study, the conjugated dienes 1,3-butadiene (BD), 2-methyl-1,3-butadiene (isoprene), and 2,3-dimethyl-1,3-butadiene (DMB) have been oxidized by photoexcited NO_2 in the cryogenic argon matrices. The mechanism and the substituent effect on reactivity have been investigated.

Experimental Section

Light irradiation was conducted directly with an Ar^+ laser (Spectra Physics, Stabilite 2016) or with an Ar^+ pumped CW dye laser (Spectra Physics, Model 375B). All-lines operation of the Ar^+ laser emits light mainly at 488 and 515 nm. Rhodamine 6G was used as the laser dye. Laser power was measured with a power meter (Spectra Physics, Model 404). The dye laser wavelength was calibrated with a monochromator (JASCO, Model CT-10). The UV photolysis was conducted with a high-pressure Hg lamp (Wacom, BM-501S, 500 W).

IR spectra were measured in the 4600–600-cm⁻¹ range with 0.5-cm⁻¹ resolution by a JASCO 8000S Fourier transform infrared spectrometer using a liquid-nitrogen-cooled MCT detector. Each spectrum was obtained by scanning over 100 times. A closed-cycle helium cryostat (Cryogenic Technology Inc., Model 21 Cryodyne) controlled the temperature of the matrix.

1,3-Butadiene (Takachiho, 99.0%) and Ar (Takachiho, 99.9999% purity) were used without further purification. NO_2 (Sumitomo Seika, pure grade) was purified by freeze-pump-

0.19 NO -0.19

Figure 1. Infrared difference spectrum upon the $582 \text{-nm} (500 \text{ mW cm}^2)$ irradiation of a matrix of BD/NO₂/Ar (=10/1/100) for 10 h. The main bands due to 3-butenyl nitrite radicals are indicated by "I".

thaw cycles at 77 and 193 K. Isoprene (Wako Pure Chemical Ind., Ltd.) and 2,3-dimethyl-1,3-butadiene (Tokyo Kasei GR) were used after freeze-pump-thaw cycles at 77 K. Conjugated dienes and NO₂ were diluted independently with argon to the diene/Ar and NO₂/Ar ratios of 10/50 and 1/50, respectively. Samples were codeposited on a CsI window at 16 K. Ethenyloxirane (Aldrich, 98%), 2,2'-bioxirane (Aldrich, 97%), 2-ethenyl-2-methyloxirane (Aldrich, 95%), 3-buten-2-one (Tokyo Kasei EP), and 2-butenal (Tokyo Kasei GR) were used as authentic samples for product identification. *m*-Chloroperbenzoic acid (Wako Pure Chemical Ind., Ltd. practical grade) was used to synthesize the oxirane product for identification.

Results

1,3-Butadiene/NO₂/Ar. The main bands observed in the FT-IR spectrum of the reactant matrix BD/NO₂/Ar (=10/1/100) could easily be identified with the bands reported for 1,3-butadiene¹⁰ and NO₂. The spectrum also contained additional weak bands due to N₂O₄ (NO₂ dimer) and N₂O₃ (NO₂ + impurity NO).^{2,11-14} Figure 1 shows the difference spectrum upon the

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 TABLE I:
 FTIR Spectra of Photoproducts Observed with

 Visible Laser Irradiation of 1,3-Butadiene/NO2/Ar

frequency.	irradiation ^a			
cm ⁻¹	intensity ^b	582 nm	all lines ^c	species
1872	24	+	+	NO
1735	ndd		+	A ^{e} (overlapped with N ₂ O ₄)
1661	80	+	-	I.
1475	2		+	Og
1441	6	+	+	0
1427	3	+	+	S ^h
1415	3		+	
1397	2	+	+	S
1348	2		+	0
1242	3		+	0
1236	10	+	-	I
1196	0.9		+	0
1136	2		+	0
1130	5	+	-	Ι
1090	1	+	+	S
1051	1		+	
1023	3		+	
995	1	+	+	S
989	10		+	0
966	2		+	0
962	19	+	-	I
921	nd	+	+	O (overlapped with S)
821	12		+	0
806	25	+	-	I
781	100	+	-	I

^a Signs of + and – indicate the positive and negative changes, respectively, in the difference spectra upon the laser irradiation. ^b Intensity is normalized to the 781-cm⁻¹ intensity. ^c "All lines" means the irradiation of all lines from the Ar⁺ laser. ^d Not determined. ^e Symbol "A" denotes 3-butenal. ^f Symbol "I" denotes 3-butenyl nitrite radicals. ^g Symbol "O" denotes ethenyloxirane. Identified by the authentic sample. ^h Symbol "S" denotes the second stable conformer of 1,3-butadiene.

582-nm laser irradiation for 10 h. The positive and negative absorptions indicate the growth and depletion, respectively, of the reactants, intermediates, or products during this irradiation period. The bands due to BD and NO₂ are observed as negative bands, while many new positive bands appear, especially two strong bands around 1660 and 780 cm⁻¹. This observation means that some photochemical reaction actually proceeds upon the 582-nm irradiation, although the wavelength is much longer than the threshold wavelength (398 nm) of NO₂ leading to the NO-(X²II) + O(³P) dissociation. In addition, the photoisomerization of N_xO_y^{2,13} and the growth of N₂O₄ were observed, especially during the first 30-min irradiation period.

The first column of Table I displays the frequencies and intensities of the positive bands due to the intermediate and products generated by the photochemical reactions of NO_2 + BD. Relative intensities of the bands at 1661, 1236, 1130, 962, 806, and 781 cm⁻¹, labeled "I" in Figure 1, remain constant during the irradiation period. Possibly, these absorption bands could be attributed to a single photoproduct.

After the 582-nm laser (500 mW cm⁻²) irradiation for 10 h, the reaction matrix containing the intermediate and products was further irradiated with the Ar⁺ laser (all lines, 80 mW cm⁻²) for 1 min. Figure 2 shows the difference spectrum upon the Ar⁺ laser irradiation for 1 min subsequent to the 582-nm irradiation for 10 h. The bands labeled "I" disappear quickly (negative bands), while the bands labeled "A", "O", and "NO" appear in turn (positive bands). Judging from the short irradiation period of the Ar⁺ laser of 1 min, the positive bands in Figure 2 can be considered to be predominantly due to the products yielded by the photolysis of the accumulated intermediate species I. In other words, species I photodissociates into species A and NO or into species O and NO.

Isoprene/NO₂/Ar. Figure 3 shows the difference spectrum upon the 582-nm laser (500 mW cm⁻²) irradiation of a matrix of isoprene/NO₂/Ar (=10/1/100) for 7 h. The peak frequencies



Figure 2. Infrared difference spectrum upon the 488/515-nm Ar ion laser (80 mW cm⁻²) irradiation of a matrix of BD/NO₂/Ar (=10/1/100) for 1 min subsequent to the 582-nm irradiation for 10 h. The main bands due to ethenyloxirane and 3-butenal are indicated by "O" and "A", respectively.



Figure 3. Infrared difference spectrum upon the 582-nm (500 mW cm⁻²) irradiation of a matrix of isoprene/NO₂/Ar (=10/1/100) for 7 h. The main bands due to methylbutenyl nitrite radicals are indicated by "I".

and relative intensities are listed in the first and second columns, respectively, of Table II. New positive bands appeared at 1657, 1230, 1138, 823, 787, and 774 cm⁻¹ and can be attributed to the reaction intermediate produced by a reaction of isoprene and photoexcited NO₂. Figure 4 shows the difference spectrum upon the subsequent Ar^+ laser (all lines, 100 mW cm⁻²) irradiation for 1 min. The absorbance changes are summarized in the fourth column of Table II. The spectrum clearly shows the depletion at bands assigned to the reaction intermediate I and the growth of bands corresponding to the final products A, O, and NO.

2,3-Dimethyl-1,3-butadiene/NO₂/Ar. Figure 5 shows the difference spectrum upon the 582-nm laser (500 mW cm⁻²) irradiation of a matrix of DMB/NO₂/Ar (=10/1/100) for 7 h. The frequencies and relative intensities are listed in the first and second columns of Table III. As in the cases of BD and isoprene, two strong bands labeled I at 1657 and 775 cm⁻¹ can be attributed to the reaction intermediate. Three bands labeled O at 1175, 1070, and 865 cm⁻¹ are clearly discernible. Figure 6 shows the difference spectrum upon the Ar⁺ laser (all lines, 100 mW cm⁻²) irradiation for 5 min subsequent to the 582-nm laser irradiation for 7 h. Absorbance changes are summarized in the fourth column of Table III.

Discussion

Identification of Final Products. In the $BD/NO_2/Ar$ system (Figure 2 and Table I), a group of absorption bands labeled O are attributed to ethenyloxirane in comparison with the matrix isolation infrared spectrum of the authentic sample. The 1735-cm⁻¹ band labeled A lies in the C=O stretch region of

 TABLE II:
 FTIR Spectra of Photoproducts Observed with

 Visible Laser Irradiation of Isoprene/NO2/Ar

frequency,	irradiation ^a			
cm ⁻¹	intensity ^b	582 nm	all lines	species
1872	32	+	+	NO
1737	nd¢	+	+	A^d (overlapped with N ₂ O ₄)
1657	100	+	-	I
1457	6	+	+	
1340	2		+	Of
1230	3	+		I
1138	3	+	-	I
1115	2	+	+	0
1092	3		+	0
1073	4	+	+	0
1058	1	+	+	0
1033	2	+	+	
1014	2	+		
983	6	+	+	0
945	4	+	+	
930	3		+	0
925	3	+		
885	10		+	0
823	3	+	-	I
817	2		+	0
787	48	+	-	Ι
774	58	+	-	Ι

^aSigns of + and – indicate the positive and negative changes, respectively, of the products upon the laser irradiation. ^b Intensity is normalized to the 1657-cm⁻¹ intensity. ^c Not determined. ^d Symbol "A" denotes 2-methyl-3-butenal or 3-methyl-3-butenal. ^e Symbol "I" denotes methylbutenyl nitrite radicals. ^f Symbol "O" denotes 2-ethenyl-2-methyloxirane which was identified by the authentic sample.



Figure 4. Infrared difference spectrum upon the 488/515-nm Ar ion laser (100 mW cm⁻²) irradiation of a matrix of isoprene/NO₂/Ar (=10/1/100) for 1 min subsequent to the 582-nm irradiation for 7 h. The main band due to methyl-3-butenal is indicated by "A".

aldehyde and ketone.¹⁵ 2-Butenal, 3-butenal, and 3-buten-2-one will be candidates for species A. The C=O stretch of α,β unsaturated aldehyde and ketone has in general the vibrational frequencies below 1700 cm⁻¹.¹⁵ The authentic samples of 2-butenal and 3-buten-2-one have the C=O stretch frequencies of 1700 and 1690 cm⁻¹, respectively, which do not accord with 1735 cm⁻¹ for species A. Hence, species A is tentatively assigned to 3-butenal. Weak bands still remain unassigned in Tables I-III.

The Ar⁺ laser (all lines) irradiation of a matrix of BD/NO₂/ Ar (=10/1/100) was attempted in order to investigate whether the monoepoxide product (ethenyloxirane) is further oxidized to diepoxide (2,2'-bioxirane) or not. The photochemical products were only ethenyloxirane, 3-butenal, and NO. Next, a mixture of commercial ethenyloxirane and NO₂ (ethenyloxirane/NO₂/ Ar = 10/1/100) was photolyzed with the dye laser (>575 nm) and the Ar⁺ laser, but no photochemical reaction occurred. On the other hand, the 300–370-nm light irradiation by a highpressure Hg lamp induced the reaction to produce 2,2'-bioxirane, which was identified by the authentic sample. The mechanism of this photooxidation reaction is not clear yet, but probably the



Figure 5. Infrared difference spectrum upon the $582\text{-nm}(500 \text{ mW cm}^2)$ irradiation of a matrix of DMB/NO₂/Ar (=10/1/100) for 7 h. The main bands due to 2,3-dimethyl-3-butenyl nitrite radical, 2-methyl-2-(1-methylethenyl)oxirane, and 2,3-dimethyl-3-butenal are indicated by "I", "O", and "A", respectively.

TABLE III: FTIR Spectra of Photoproducts Observed with Visible Laser Irradiation of DMB/NO₂/Ar

frequency, cm ⁻¹		irradiation ^a		
	intensity ^b	582 nm	all lines	species
1872	41	+	+	NO
1731	nd¢	+	+	A^d (overlapped with N ₂ O ₄)
1657	100	+	_	Ie
1470	4	+		
1462	4		+	
1442	8	+		
1320	6	+	+	
1175	15	+	+	O,
1070	13	+	+	0
910	10		+	
865	21	+	+	0
775	92	+	-	I

^a Signs of + and – indicate the positive and negative changes, respectively, of the products upon the laser irradiation. ^b Intensity is normalized to the 1657-cm⁻¹ intensity. ^c Not determined. ^d Symbol "A" denotes 2,3-dimethyl-3-butenal. ^e Symbol "I" denotes 2,3-dimethyl-3-butenyl nitrite radical. ^f Symbol "O" denotes 2-methyl-2-(1-methylethen-yl) oxirane which was identified by the synthesized sample.



Figure 6. Infrared difference spectrum upon the 488/515-nm Ar ion laser (100 mW cm⁻²) irradiation of a matrix of DMB/NO₂/Ar (=10/1/100) for 5 min subsequent to the 582-nm irradiation for 7 h.

O + monoepoxide \rightarrow diepoxide reaction might be responsible for this observation. Thus, it is concluded that monoepoxide cannot be oxidized further to diepoxide through the visible light induced reaction with NO₂.

In addition to the oxidation of BD, the isomerization of BD from the stable *s*-trans form to the second stable conformer was also observed. The structure of the second stable conformer of BD has been studied experimentally and theoretically.^{10,16-25} IR

TABLE IV: Summary of Final Products Formed by Visible Laser Irradiation of Diene/NO₂/Ar Matrices



^a R = H and/or CH₃. ^b Denoted by "O" in figures and tables. ^c Denoted by "A" in figures and tables.

bands at 1427, 1397, 1090, and 995 cm⁻¹ listed in Table I can be assigned to those of the second stable conformer of BD, although the 914-cm⁻¹ band of the second conformer is overlapped with the band of a product (ethenyloxirane). The possibility that the IR bands at 1427, 1397, 1090, and 995 cm⁻¹ are due to the final products (A, O, and NO) can be excluded based on the following reason: The four bands grew with the light irradiation at 615 or 595 nm, while the bands due to the final products did not appear with the irradiation of light longer than 582 nm. At room temperature, 97% of BD exists as the s-trans form.¹⁶ The second stable conformer can be obtained by the high-temperature deposition through an oven or the photoexcitation of BD into the S_1 state. However, in this experiment, the reaction on the S_1 surface does not take place since the S_1 state of BD lies about 5.64 eV above the ground state. On the other hand, the barrier of a rotation from the ground state to the second stable conformer is only 5 kcal mol⁻¹ on the S_0 surface.¹⁷ The heat released from the relaxation of photoexcited NO₂ might induce this isomerization.

In the isoprene/NO₂/Ar system (Figure 4 and Table II), the final product labeled O is assigned to 2-ethenyl-2-methyloxirane. The 1737-cm⁻¹ band lies in the C=O stretch region of unconjugated aldehyde. 2-Methyl-3-butenal or 3-methyl-3-butenal might be responsible for the 1737-cm⁻¹ band.

In the DMB/NO₂/Ar system (Figure 6 and Table III), the final product labeled O is assigned to 2-methyl-2-(1-methyl-ethenyl)oxirane. This oxirane was identified after being synthesized by oxidation of DMB with *m*-chloroperbenzoic acid in the vacuum. The 1731-cm⁻¹ absorption band lies in the C=O stretch region of unconjugated aldehyde, and it is tentatively assigned to 2,3-dimethyl-3-butenal on the analogy of the BD/NO₂/Ar system.

In Table IV we summarize the final products (except NO) detected in all three photochemical systems. They are identified as ethenyloxirane (or its methyl substitutes) and 3-butenal (or its methyl substitutes).

Identification of Intermediates. On the basis of the final products (ethenyloxirane, 3-butenal, and NO) discussed above, the reaction intermediates labeled I are expected to be an adduct of diene and NO₂. In the gas phase, conjugated dienes react with NO₂ thermally to produce nitro compounds.^{26,27} However, this possibility can be ruled out based on the following reason: nitro compounds should have the absorption bands around 1550 and 1350 cm⁻¹,¹⁵ yet the intermediate species I have the strong absorption bands around 1660 and 780 cm⁻¹.

More plausible candidates for species I will be nitrite compounds having the structure of C-O-N=O skeletons. Alkyl nitrites have their IR absorptions around 1650 cm^{-1} (N=O stretch), 800 cm^{-1} (N-O stretch), and 600 cm^{-1} (O-N=O bend).²⁸ Although they have *trans* and *cis* forms with respect to the central O-N bond, only methyl and ethyl nitrites are known to be stable in both the *cis* and *trans* forms.^{28,29} Larger alkyl nitrites are predominantly stable in the *trans* forms.²⁸ Actually, alkyl nitrite radicals formed SCHEME I





in the visible laser irradiation of alkene/NO₂/Ar matrices are predominantly in the *trans* form.¹⁻³ Thus, the intermediate species I formed in the BD/NO₂/Ar matrix are concluded to be butenyl nitrite radicals in the *trans* form.

Similarly in the isoprene/ NO_2 /Ar and DMB/ NO_2 /Ar systems, the intermediate species labeled I are concluded to be methylbutenyl and dimethylbutenyl nitrite radicals, respectively.

Photochemical Reaction Mechanism. The visible light excitation of diene-NO₂ reactant pairs has been found to cause an oxygen atom transfer from NO₂ to diene to form the oxirane biradical, which is similar to the photochemical reactions observed in the alkene/NO₂/Ar systems.¹⁻⁹ This biradical undergoes three possible reactions: (1) the ring closure of the biradical to give oxirane, (2) the 1,2-hydrogen migration to produce aldehyde. and (3) the recombinaton with NO (the cage partner in the matrix) to yield the nitrite radical. Two isomers can be considered for the nitrite radical (Scheme I). Isomer 1 is a nitrite radical having a C-O bond at the terminal position of the butadiene skeleton and is therefore stabilized by allylic resonance. Isomer 2 is a nitrite radical having a C-O bond at the inner C atom of the butadiene skeleton and is unstable due to the nonresonant structure. We have already stated that the π electrons in the C=O bond of the final aldehyde product do not conjugate with those in the C=C double bond. If the intermediate nitrite radical has a form of isomer 1, the aldehyde is certainly of the unresonant form, 3-butenal. On the other hand, resonant ketone would be formed by the secondary photolysis of isomer 2. Therefore, we believe the nitrite radical is isomer 1: that is, the reaction sites are at the terminal C atoms of butadiene.

The laser irradiation of a $BD/NO_2/Ar$ or $DMB/NO_2/Ar$ mixture resulted in detection of one kind of nitrite radical (the N–O frequencies at 781 cm⁻¹ for BD and at 775 cm⁻¹ for DMB). Two kinds of reaction sites at the terminal carbons on C(1) and C(4) can be expected for the isoprene/NO₂ system. Actually, in this system, we detected two bands corresponding to the N–O stretch, which implies that two kinds of nitrite radicals are formed: the band at 787 cm⁻¹ due to the nitrite radical having a C(4)–ONO bond and the band at 774 cm⁻¹ due to the radical having a C(1)–ONO bond.

The reaction rates were measured by the absorbance changes of the intermediate nitrite radical and the final product NO. The reaction mechanism is assumed to involve an oxirane biradical that undergoes rapid stabilization. The final products are yielded through two reaction paths, namely, the one- and the two-photon paths (Scheme II). Symbols R, I, and P denote the reaction pair, the nitrite radical, and the products, respectively. The $I \rightarrow P$ reaction stands for the photolysis of I. All three rate constants $(k_1, k_2, \text{ and } k_3)$ are analyzed as the pseudo-first-order reactions. The differential equations give the following integration form:²

$$A_{\rm I} = A_0 \frac{\epsilon_{\rm I}}{\epsilon_{\rm R}} \frac{k_1}{k_2 - (k_1 + k_3)} \{ e^{-(k_1 + k_3)t} - e^{-k_2 t} \}$$
(1)

$$A_{\rm P} = A_0 \frac{\epsilon_{\rm P}}{\epsilon_{\rm R}} \bigg[1 + \frac{1}{k_2 - (k_1 + k_3)} \{ k_1 \mathrm{e}^{-k_2 t} - (k_2 - k_3) \mathrm{e}^{-(k_1 + k_3) t} \} \bigg]$$
(2)



Irradiation time / min

Figure 7. Time evolution of the nitrite radical yields with the three different light irradiations of a matrix of BD/NO₂/Ar (=10/1/100) at 582 nm (\bigcirc), 595 nm (\bigcirc), and 615 nm (\triangle). The kinetic parameters used for the simulation are as follows in units of 10⁻³ min⁻¹: $k_1 = 13$, $k_2 = 0$, $k_3 = 5.8$ for 582 nm; $k_1 = 6.7$, $k_2 = 0$, $k_3 = 0$ for 595 nm; $k_1 = 4.4$, $k_2 = 0$, $k_3 = 0$ for 615 nm.

Here, A and ϵ denote absorbance and absorption coefficient, respectively. Subscripts R, I, and P refer to reactant pair, intermediate, and product, respectively. A_0 denotes the absorbance of the reactant pair before the irradiation, and the A_0/ϵ_R ratio corresponds to the concentration of the reactant pair.

We consider the wavelength dependence of the reactions in the $BD/NO_2/Ar$ system. With the red light irradiation at 615 and 595 nm, it was difficult to observe the growth of final products. Therefore, one can assume that $k_2 = k_3 = 0$ for the 615- and 595-nm irradiation. An estimation of the k_1 values is possible by a single exponential fitting of eq 1 to the absorbance changes of the butenyl nitrite radical (monitored at 781 cm⁻¹). In general, the rate constants k_1 , k_2 , and k_3 are calculated by the nonlinear least-squares method using eqs 1 and 2. The best fit curves are displayed as lines in Figure 7. The values of the rate constant k_1 , in units of 10^{-3} min⁻¹, are determined to be 13 ± 0.1 , 6.7 ± 0.1 1.1, and 4.4 ± 1.8 with the irradiation of 582, 595, and 615 nm, respectively. The rate constant k_1 becomes larger as the laser wavelength becomes shorter. The laser intensities for three wavelengths were controlled to be constant. In this wavelength region, the absorption spectrum of NO₂ is complex³⁰ due to the interaction of four electronic states: \tilde{X}^2A_1 , \tilde{A}^2B_2 , \tilde{B}^2B_1 , and \tilde{C}^2A_2 . However, the absorbances at these three wavelengths are reported to be almost the same.³¹ Therefore, the change in the k_1 value is mainly attributed to the variation in the reaction quantum yield. It is clearly shown that the photochemical reaction quantum yield becomes larger with increasing energy of the photons absorbed by the reactant pairs.

The methyl substituent effect on the rate constant is considered below. Nonlinear least-squares fitting of 1 and 2 to the experimental data upon the 582-nm laser irradiation gives the kinetic parameters listed in Table V. It shows a tendency that the rate constants k_2 and k_3 become larger as the number of the methyl substituents is increased. The rate constants are expressed by the products of the absorption coefficient ϵ , the reaction quantum yield ϕ , and the laser intensity I: $k_2 = \epsilon_1 \phi_2 I$ and $k_3 =$ $\epsilon_{NO_2}\phi_3 I$. Since the same laser intensity and wavelength were used in all three cases, the difference in the rate constants reflects the variations in the reaction quantum yield. The increase of the k_3 value with methyl substitution may be explained by a model according to which the oxirane biradical is stabilized by the substitution. The consequence is more excess internal kinetic energy for surpassing the barrier to epoxide/aldehyde formation. The monoepoxide is efficiently produced with the red light

TABLE V: First-Order Rate Constants Calculated by the Nonlinear Least-Squares Method^a

	$k_1,$ 10 ⁻³ min ⁻¹	k ₂ , 10 ⁻³ min ⁻¹	k3, 10 ⁻³ min ⁻¹	$A_0/\epsilon_{\rm R},$ 10 ⁻³ mol ⁻¹ L cm ⁻¹ c	€1∕€p ^b
BD	13 ± 0.1	0 ± 0.1	5.8 ± 1.0	54 ± 1.6	3.4
isoprene	9.9 ± 1.0	0.1 ± 0.2	7.5 ± 1.2	40 ± 1.3	3.1
DMB	11 ± 1.4	1.4 ± 0.3	13 ± 2.2	46 ± 1.4	2.4

^a $A_{\rm I}$ was measured at 1661 cm⁻¹ for BD, 1657 cm⁻¹ for isoprene, and 1657 cm⁻¹ for DMB. $A_{\rm P}$ was measured at 1872 cm⁻¹. ^b The ratio $\epsilon_{\rm I}/\epsilon_{\rm P}$ was obtained by comparing the absorbance at 1872 cm⁻¹ (NO) with those at 1661, 1657, and 1657 cm⁻¹ (nitrite radicals corresponding to BD, isoprene, and DMB, respectively). The absorbance changes are obtained from the difference spectrum upon the Ar⁺ laser (all lines) irradiation for 1 min subsequent to the 582-nm irradiation for 10 h. ^c The value $A_0/\epsilon_{\rm R}$ depends on the amount of the reactant pairs.

irradiation in the DMB/NO₂ system (Figure 5), which is different from the observation in the BD/NO_2 and isoprene/NO₂ systems.

In the alkene/NO₂ systems, large k_2 values have been reported. For example, the k_2 value is 10 times larger than the values of k_1 and k_3 . In the diene/NO₂ systems, the k_2 values are negligibly small compared to those of k_1 and k_3 (Table V). It is not easy to compare the result of the diene/ NO_2 experiment with that of the alkene/NO₂ experiment, because of the difference in the experimental conditions. In the trans-2-butene/NO₂ system, the intermediate grows upon the 590-nm (405 mW cm⁻²) irradiation but decays upon prolonged irradiation as shown in Figure 4 of ref 2. The decay is caused by the photolysis of the intermediate. However, in the BD/NO_2 system the decay of the intermediate was not observed even upon the 582-nm (500 mW cm⁻²) irradiation, as shown in Figure 7. The absorption coefficients of the nitrite radicals formed in the diene/NO₂ systems will be expected to be comparable or even larger than those in the alkene/ NO_2 systems. Therefore, it is concluded that the quantum yield for dissociation of nitrite radicals is much larger in alkene/ NO_2 systems than in diene/NO₂ systems. For the trans-2-butene/ NO₂ system,² the photodissociation process is expressed by reaction 3. Similarly for the BD/NO_2 system, the photodissociation process is expressed by reaction 4.³² The difference in the ΔH_r values might be a reason why the photodissociation yields of nitrite radical are much smaller in the diene/NO₂ systems than in the alkene/NO₂ systems.

$$\Delta H_r = -14 \text{ kcal mol}^{-1}$$

$$\Delta H_r = +13 \text{ kcal mol}^{-1}$$

$$\Delta H_r = +13 \text{ kcal mol}^{-1}$$
(4)

Conclusions

Matrix isolation experiments were performed to study the photochemical reactions of NO₂ with conjugated dienes. The IR spectra showed the formation of nitrite radicals as the reaction intermediate and oxiranes and aldehydes as the final products. The nitrite radicals are stabilized due to the allyl resonance. The reaction scheme is proposed. The reactions are initiated by the formation of undetectable short-lived oxirane biradical and NO due to visible light induced O atom transfer from NO₂ to the conjugated dienes with the selective attack of the terminal carbon atom. (1) The recombination of oxirane biradicals and neighboring NO gives the nitrite radicals as the photochemical intermediate. (2) The ring closure of the biradicals leads to the formation of oxiranes. (3) The intramolecular H atom transfer of biradicals leads to the formation of aldehydes. The visible photolysis of the nitrite radicals gives rise to oxirane, aldehyde, and NO. The reaction rates are derived by measuring the

absorbance changes of the products upon the 582-nm irradiation. The methyl substitution of BD enhances the formation rate of the final products via the direct path.

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References and Notes

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(32) To estimate the heat of reaction (ΔH_t) , we used the following thermodynamic data: the standard enthalpies of formation for H, NO2, BD, NO, ethenyloxirane, and methyl allyl radical to be 52.1, 33 7.9, 33 26.1, 34 21.6, 33 10.0,35 and 30.433 kcal mol-1, respectively, and the dissociation energy of the C-H bond for the methyl allyl radical and the C-O bond for the butenyl nitrite radical to be 95^{36} and 62^{37} kcal mol⁻¹, respectively.

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- (37) Calculated using the heats of formation of $n-C_4H_9$ (18.5 kcal mol⁻¹), n-C4H9ONO (-35.8 kcal mol-1), and NO2 (7.9 kcal mol-1).