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# Red light-induced reaction of $NO_2$ with 2,3-dimethyl-2-butene in a low-temperature argon matrix

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**Abstract**—Red light-induced oxygen atom transfer from $NO_2$ to 2,3-dimethyl-2-butene has been investigated in a low-temperature argon matrix. The IR spectra of a reaction intermediate indentified as an alkyl nitrite radical and two final products, tetramethyloxirane and 3,3-dimethyl-2-butanone (pinacolone), were observed. From analysis of the absorbance growth of the IR bands, first-order rate constants were determined by least-square fitting. Based on these results and those of our earlier works on $NO_2$ photoreactions with other alkenes, a reaction mechanism is proposed that involves oxygen atom transfer from $NO_2$ to the C=C bond of 2,3-dimethyl-2-butene to give a short-lived singlet oxirane biradical. Alkyl nitrite radical is produced by a recombination of the transient biradical with NO trapped in the cage of the matrix. Tetramethyloxirane and pinacolone emerge from secondary photolysis of the trapped alkyl nitrite radical.

## INTRODUCTION

WE HAVE recently reported studies on visible light-induced reactions of $NO_2$ with alkenes in low-temperature matrices [1–10]. The proposed reaction mechanism involves oxygen atom transfer from photoexcited $NO_2$ to the alkene to produce a transient oxirane biradical. The biradical is stabilized either by recombination with NO to yield an alkyl nitrite radical, by ring closure to form an epoxide or by rearrangement to give a carbonyl compound. These products are formed following absorption of a single visible photon by alkene–$NO_2$ pairs in the cage of the matrix (one-photon path). IR spectra of $^{18}O$-, $^{15}N$- and D-labelled species of a number of alkyl nitrite radicals have been measured to establish the structure of these radicals [1–10]. In the case of *trans*-2-butene [1], for example, we observed the IR spectra of $^{18}O$ isotopic species of the butyl nitrite radical with a *trans* conformation about the central C–C bond and explained successfully the isotope shifts in terms of the proposed structure. From analysis of the absorbance growth kinetics of the IR bands for the butyl nitrite radical and the final product, *trans*-2,3-dimethyloxirane, a second photoreaction was discerned. It involves secondary photolysis of the trapped nitrite radical to yield *trans*-2,3-dimethyloxirane (two-photon path). No other product was detected in the IR spectra of $NO_2$ photoreaction with *trans*-2-butene.

In the present study, red light-induced reaction of $NO_2$ with 2,3-dimethyl-2-butene in an argon matrix is reported. The results are compared with those of $NO_2$ photoreactions with other small alkenes, such as ethylene and its methyl substituted derivatives. We have focused our interest on the effects of substitution of methyl groups on the vibrational spectra of nitrite radicals and final oxidation products, as well as the photochemical rate constants and threshold wavelength of these alkene + $NO_2$ systems.

## EXPERIMENTAL

A diagram of the experimental system used is shown in Fig. 1. 2,3-Dimethyl-2-butene (Aldrich) and $NO_2$ (Sumitomo Seika Co.) were diluted with argon gas (Takachiho Co.) in separate sample holders. Both gas mixtures were co-deposited through stainless steel tubes onto a CsI window held at 20 K. Deposition rates were about 1 mmol $h^{-1}$ and deposition time was about 1 h. Two kinds of mixing ratios of the gases were chosen; one was 2,3-dimethyl-2-butene–$NO_2$–Ar = 2.5 : 1.0 : 100 (here termed "regular sample") and the other was 2.5 : 1.0 : 400 ("dilute sample"). The cryostat used was closed cycle helium refrigeration (Cryogenic Technology Inc., Model 21). Chemical

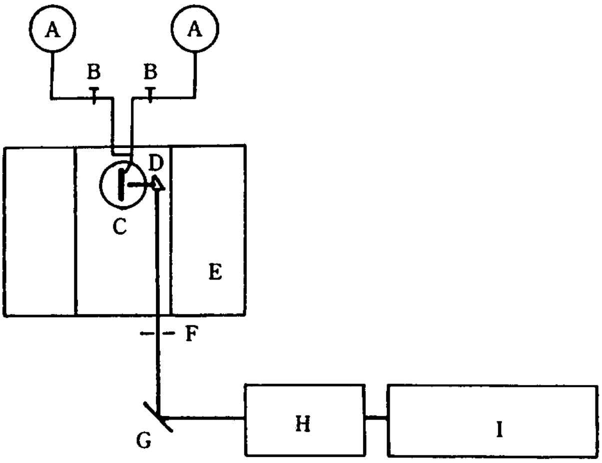


Fig. 1. Diagram of the experimental set-up. (A) Bulbs containing $NO_2$–Ar and 2,3-dimethyl-2-butene–Ar gas mixtures. (B) Needle valves. (C) Caesium iodide cold plate held at 20 K in a vacuum chamber. (D) Prism. (E) FTIR spectrophotometer, JASCO-8000S. (F) Aperture. (G) Mirror. (H) Dye laser, Spectra Physics Model 375B. (I) Argon ion laser, Spectra Physics Model 2016.

reaction was monitored by IR spectroscopy using a JASCO FT/IR-8000S spectrophotometer. Spectra were taken at a resolution of 0.5 $cm^{-1}$. The diameter of the IR probe beam at the matrix was 1 mm.

Matrix samples were irradiated with light from a cw dye laser (Spectra Physics Co. Model 375B) pumped by an argon ion laser (Spectra Physics Co. Model 2016) using the dye Rhodamine 590 (Exciton). The dye laser wavelength was calibrated with an accuracy of 0.1 nm by a monochromator (JASCO, Model CT-10). The laser power was monitored before and after each irradiation period by a power meter (Spectra Physics Co., Model 404).

## RESULTS

### *Spectra of reactants*

Figure 2 shows the IR spectrum of a "regular" matrix sample (2,3-dimethyl-2-butene–$NO_2$–Ar, 2.5 : 1.0 : 100) before irradiation. Two bands at 1605 and 749 $cm^{-1}$ labelled N in the figure are due to $NO_2$. Other bands designated as B are due to 2,3-dimethyl-2-butene, whose wavenumbers correspond to the reported values obtained in the gas phase to within 10 $cm^{-1}$ [11]. Other weak bands are due to $NO_2$ dimer, $N_2O_4$, or a small amount of impurity, $N_2O_3$; spectroscopic details of these species have been reported previously [1].

### *Spectra of reaction intermediate*

Figure 3 shows the spectral change of a "dilute" matrix sample (2,3-dimethyl-2-butene–$NO_2$–Ar, 2.5 : 1.0 : 400) by 635 nm laser irradiation for 25 min. As described in our previous paper [1], most of the spectral changes originate from photoisomerization of $N_2O_4$ and $N_2O_3$ under near-IR or visible irradiation. The wavenumbers and the directions of the intensity changes (decrease or increase) of $N_2O_4$ and $N_2O_3$ by red light irradiation have been reported [1]. On the other hand, five new bands appeared at 1634, 1183, 1121, 934 and 744 $cm^{-1}$. These bands seem to belong to a photoreaction intermediate, because their intensities decreased abruptly upon subsequent irradiation at shorter wavelengths, as shown in Fig. 4.

### *Spectra of final products*

Figure 4 shows spectral changes upon 570 nm laser (yellow light) irradiation for 10 min of the "dilute" matrix sample following irradiation at 635 nm (red light) for 50 min in

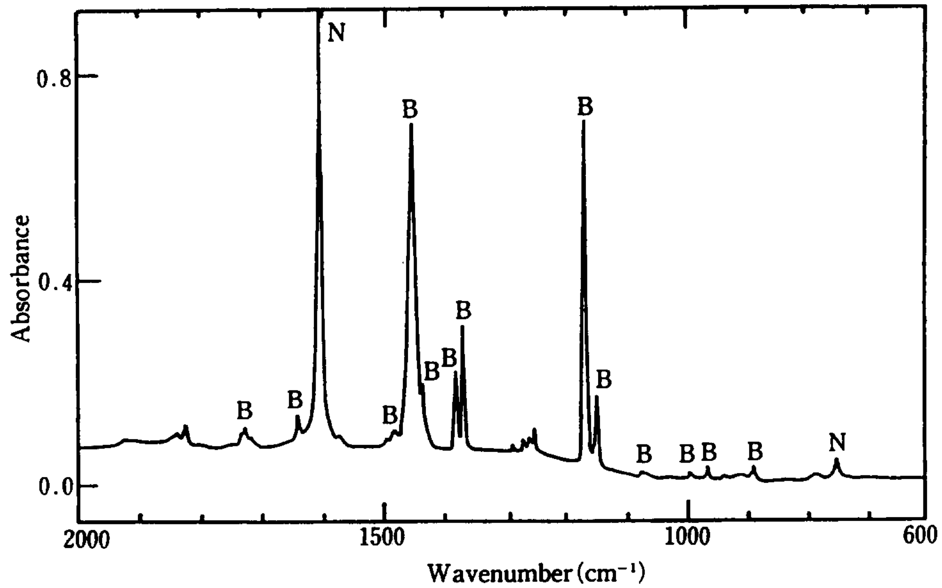


Fig. 2. IR spectrum of a "regular" matrix sample (2,3-dimethyl-2-butene–$NO_2$–Ar, 2.5 : 1 : 100) before irradiation. The symbols N and B denote bands due to $NO_2$ and 2,3-dimethyl-2-butene, respectively. Other small bands are due to $N_2O_3$ or $N_2O_4$.

order to accumulate the reaction intermediate. In Fig. 4, new bands appeared at 1872, 1717 and 1206 $cm^{-1}$, while the intensities of the five bands of the reaction intermediate decreased. The band at 1872 $cm^{-1}$ is easily assigned to NO based on our previous results on alkenes and $NO_2$ photoreactions [1–10].

In order to detect other weak bands of the final products, spectral changes of a "regular" matrix sample upon irradiation at 635 nm for 25 min were obtained. The difference spectrum is shown in Fig. 5. It is found that the bands of the reaction intermediate, designated as I, described in the previous section also increase during this irradiation period. The wavenumbers and the relative intensities of the final products, designated as K or O, are summarized in Table 1.

### *Reaction rate constants and photolysis wavelength dependence*

Figure 6 shows the photolysis wavelength dependence of the absorbance growth of an IR band of the reaction intermediate (744 $cm^{-1}$), the final product K (1717 $cm^{-1}$) and the final product O (1206 $cm^{-1}$) upon prolonged 635, 615 and 595 nm irradiation. The dye laser power was kept constant at 100 mW $cm^{-2}$ for each irradiation.

## DISCUSSION

### *Assignment of reaction intermediate*

Two strong bands at 1634 and 744 $cm^{-1}$ for the reaction intermediate shown in Fig. 3 are characteristic of a nitrite compound [12]. They can be assigned to N=O stretching and O–N stretching modes, respectively, as discussed in our previous works on alkenes and $NO_2$ photoreaction [1–10]. The other weak bands of I were assignable to skeletal stretching modes. It is concluded that the intermediate is 2,3-dimethyl-2-butyl nitrite radical.

The wavenumbers of some alkyl nitrite radicals studied by us are summarized in Table 2. The frequencies of both N=O stretching and O–N stretching modes decrease systematically as the number of methyl groups increases. This trend is also found in the case of some closed-shell nitrite compounds reported by TARTE [12].

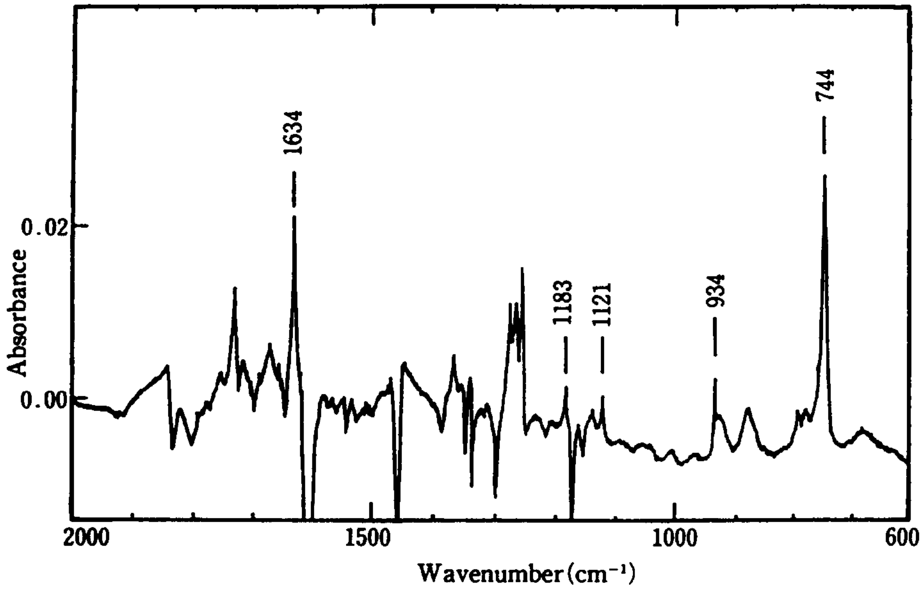


Fig. 3. Spectral change of a "dilute" matrix sample (2,3-dimethyl-2-butene–$NO_2$–Ar, 2.5:1:400) upon 635 nm laser irradiation for 25 min. Five bands at 1634, 1183, 1121, 934 and 744 $cm^{-1}$ are due to an intermediate. Other spectral changes originate from $N_xO_y$ isomerization.

## *Assignment of final products*

Both the one-photon reaction path and the two-photon reaction path must be considered in visible light-induced photoreactions between alkenes and $NO_2$ in low-temperature argon matrices. Reaction intermediates (i.e. alkyl nitrite radicals) are produced exclusively by single-photon photolysis of alkene–$NO_2$ pairs. The origin of the final products depends on the specific alkene–$NO_2$ system. The results are summarized in Table 3. In the case of *trans*-2-butene [1], only *trans*-2,3-dimethyloxirane was produced

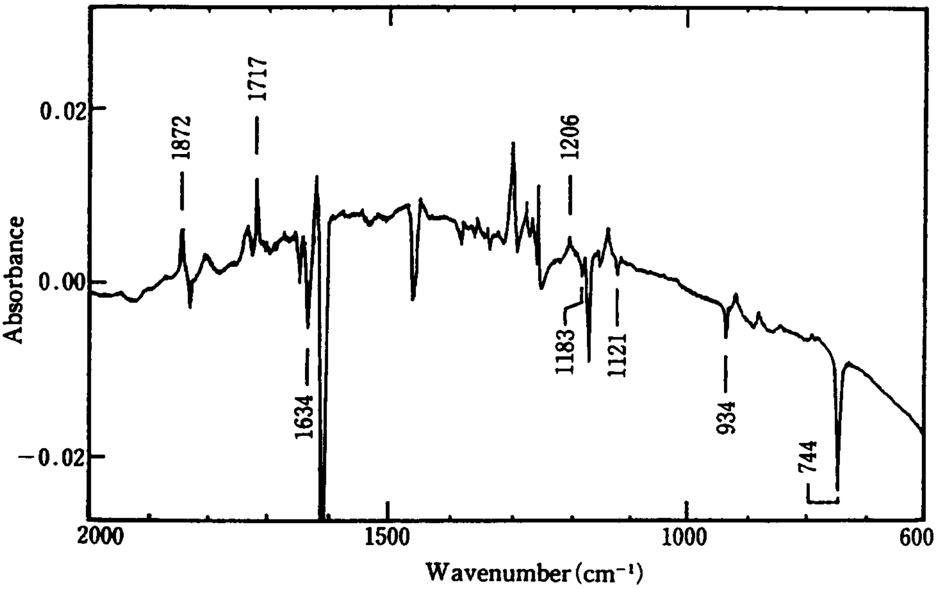


Fig. 4. Spectral changes of a "dilute" matrix sample (2,3-dimethyl-2-butene–$NO_2$–Ar, 2.5:1:400) upon 570 nm laser irradiation for 10 min after accumulation of intermediate by 635 nm laser photolysis for 50 min. Decreasing bands are due to depletion of intermediate. Increasing bands are due to the final products NO (1872 $cm^{-1}$), 3,3-dimethyl-2-butanone (1717 $cm^{-1}$) and tetramethyloxirane (1206 $cm^{-1}$).

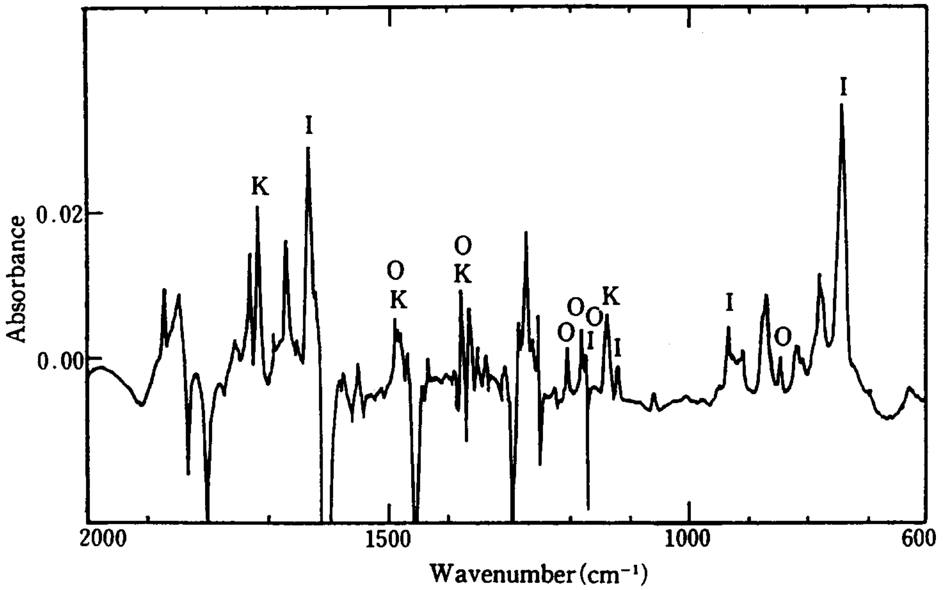


Fig. 5. Spectral change of a "regular" matrix sample (2,3-dimethyl-2-butene–$NO_2$–Ar, 2.5 : 1 : 100) upon 635 nm laser irradiation for 25 min. Increasing bands are due to an intermediate (I, nitrite radical), and final products labelled K (3,3-dimethyl-2-butanone) or O (tetramethyloxirane).

along both the one-photon and the two-photon paths. This implies that the transient oxirane biradical produced both along the one-photon path and upon photoelimination of NO from the trapped butyl nitrite radical undergoes ring closure, but no 1,2-H or -$CH_3$ migration. By contrast, in the case of *cis*-2-butene [2], *cis*-2,3-dimethyloxirane is the exclusive final product of the one-photon path, while methylpropanal is the sole product of alkyl nitrite radical secondary photolysis. This implies distinct differences in the competition between cyclization and 1,2-$CH_3$ migration, depending on whether the oxirane biradical is produced by *cis*-2-butane–$NO_2$ photolysis or by photoelimination of NO from *cis*-butyl nitrite radical. In the case of methylpropene [3], cyclization and migration of a hydrogen atom occurred along both paths. The final products were 2,2-

Table 1. Vibrational frequencies (in cm$^{-1}$) and relative intensities of final products of $NO_2$ and 2,3-dimethyl-2-butene photoreaction

| | Authentic samples | |
|---|---|---|
| Final products | Tetramethyloxirane | 3,3-Dimethyl-2-butanone |
| 1717 (1.0)† | | 1713 (1.0) |
| 1483 (0.1) | 1484 (0.2) | |
| 1480 (0.2) | | 1480 (0.2) |
| 1468 (0.1) | 1471 (0.1) | |
| 1435 (0.1) | 1438 (0.1) | 1439 (0.1) |
| 1421 (0.1) | | 1422 (0.1) |
| 1405 (0.1) | 1406 (0.1) | |
| 1381 (0.6) | 1381 (0.7) | |
| 1364 (0.3) | | 1369 (0.2) |
| 1355 (0.4) | | 1354 (0.4) |
| 1206 (0.3) | 1205 (0.3) | |
| 1173 (—)‡ | 1173 (1.0) | |
| 1138 (0.5) | 1142 (0.3) | 1139 (0.4) |
| 950 (0.1) | | 950 (0.1) |
| 849 (0.3) | 847 (0.2) | |

† Relative intensities are given in parentheses.

‡ Overlapped by the reactant, 2,3-dimethyl-2-butene.

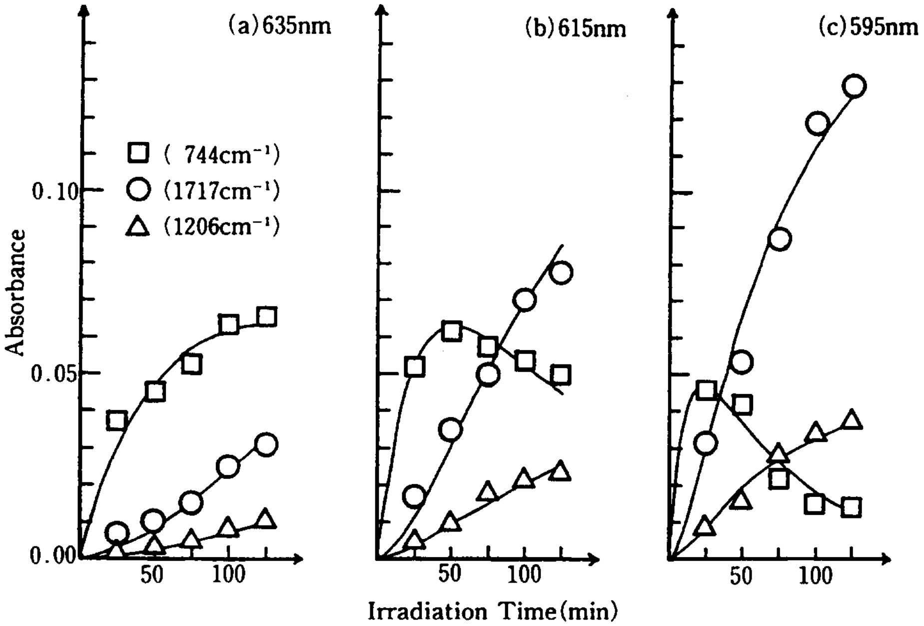


Fig. 6. Absorbance growth behaviour of IR bands of a photoreaction intermediate and two final products. Symbols □, ○ and △ denote the bands at 744 (nitrite radical), 1717 (K; 3,3-dimethyl-2-butanone) and 1206 cm$^{-1}$ (O; tetramethyloxirane). Wavelength of laser light is 635 (a), 615 (b) and 595 nm (c). Solid lines represent the calculated values using the rate constants listed in Table 4.

dimethyloxirane and methylpropanal. Based on these results, both cyclization and migration of a methyl group may occur upon visible light-induced reaction between 2,3-dimethyl-2-butene and $NO_2$. Hence, tetramethyloxirane (cyclization) and 3,3-dimethyl-2-butanone (migration of a methyl group) are the expected final products in the case of this system.

In order to confirm these assignments, the IR spectrum of 3,3-dimethyl-2-butanone, purchased from Wako Pure Chem. Ind., Ltd., was measured in an argon matrix. The mixing ratio of 3,3-dimethyl-2-butanone–Ar was 1:40. The wavenumbers and the relative intensities of 3,3-dimethyl-2-butanone were compared with those of the final products of the photoreaction between 2,3-dimethyl-2-butene and $NO_2$ presented in Table 1. It was found that the bands of species K correspond to those of 3,3-dimethyl-2-butanone within uncertainties. The relative intensities of the observed K bands are also consistent with those of the authentic 3,3-dimethyl-2-butanone spectrum.

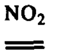
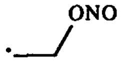
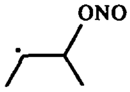
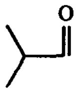
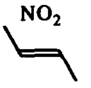
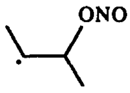
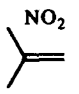
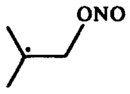
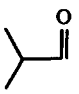
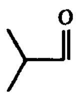
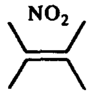
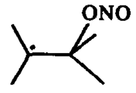
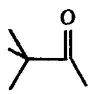
A sample of tetramethyloxirane was prepared by a general method for the synthesis of oxiranes from alkenes [13]: *m*-chloroperbenzoic acid was added to 2,3-dimethyl-2-butene frozen at liquid nitrogen temperature *in vacuo*. The temperature of the reaction mixture was elevated and the sample was kept for 15 min at room temperature. After vacuum

Table 2. Vibrational frequencies of N=O stretching and O–N stretching modes for alkyl nitrite radicals (in cm$^{-1}$)

| Reactant | N=O stretch | O–N stretch | Reference |
|---|---|---|---|
| Ethylene | 1664 | 773 | [4] |
| *Cis*-2-butene | 1652 | 772 | [2] |
| *Trans*-2-butene | 1645 | 755 | [1] |
| Methylpropene | 1644 | 754 | [3] |
| 2,3-Dimethyl-2-butene | 1634† | 744 | This work |

† Disturbed by the band of asymmetric $N_2O_3$ at 1631 cm$^{-1}$.

Table 3. Intermediate and final products of $NO_2$ and alkenes photoreaction

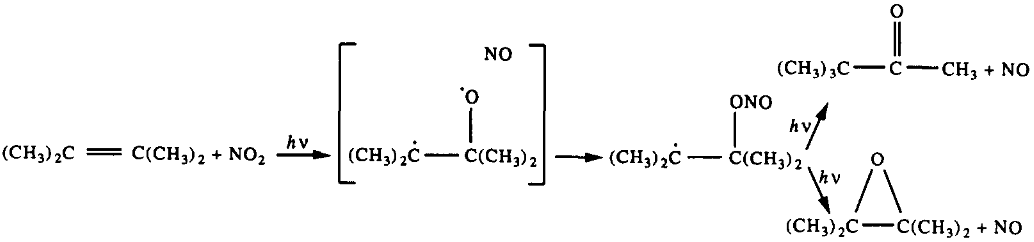
| Reactant | Intermediate | Final products<br>One-photon† | <br>Two-photon‡ | References |
|---|---|---|---|---|
|  |  |  |   | [4, 8] |
|  |  |  |  | [2] |
|  |  |  |  | [1] |
|  |  |   |   | [3] |
|  |  | |   | This work |

† Directly produced by alkene–$NO_2$ photolysis.
‡ Produced from photoexcited nitrite radical.

distillation of the sample, $^1H$ and $^{13}C$ NMR spectra were measured. Only two $^1H$ NMR peaks were observed. The chemical shifts ($\delta$) were 1.314 and 1.638 ppm. Since the former corresponds exactly to the shift of the reactant, 2,3-dimethyl-2-butene, the latter can confidently be assigned to an oxidation product. On the other hand, only four $^{13}C$ NMR peaks were observed except for the $CDCl_3$ solvent peak. Chemical shifts at 20.3 and 123.4 ppm originate from the reactant, 2,3-dimethyl-2-butene, while additional peaks at 21.1 and 62.0 ppm are due to the oxidation product. Since only one peak of the $^1H$ NMR spectrum and only two peaks of the $^{13}C$ NMR spectrum were attributable to the product, the oxidation product of 2,3-dimethyl-2-butene by *m*-chloroperbenzoic acid is assigned to tetramethyloxirane. This molecule has one set of equivalent hydrogen atoms and two sets of carbon atoms as observed. The IR spectrum of tetramethyloxirane in an argon matrix was observed. The wavenumbers and the relative intensities are compared in Table 1. Good agreement exists between photolysis products bands labelled O (Fig. 5) and those of the authentic tetramethyloxirane spectrum. It was found that all the bands of the final products of photoreaction between 2,3-dimethyl-2-butene and $NO_2$ can be assigned to NO, 3,3-dimethyl-2-butanone and tetramethyloxirane.

### *Reaction mechanism*

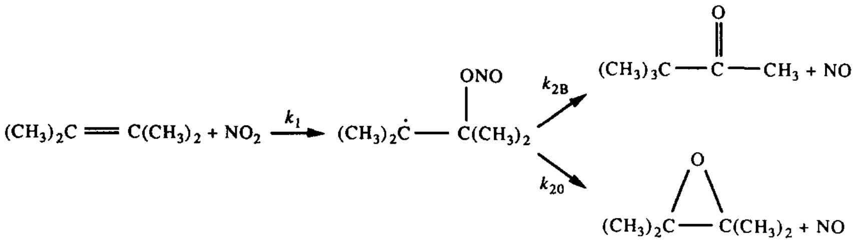
As described in our previous papers [1–10], the primary transient species of visible light-induced alkene + $NO_2$ reactions is an oxirane biradical, which is produced by transfer of an oxygen atom from photoexcited $NO_2$ to the alkene molecule under concurrent production of NO. Oxirane compounds, carbonyl compounds or nitrite radicals are produced from the transient oxirane biradical by cyclization, 1,2-migration or combination with NO, respectively (one-photon path). Carbonyl and/or oxirane products may also emerge by secondary photolysis of the alkyl nitrite radical (two-photon path). In the present system, ketone and oxirane produced along the one-photon reaction path must be negligible because there are clear induction periods in the absorbance growth curves of the IR bands for the final products, as shown in Fig. 6. Based on the assignments of the reaction intermediate and the final products, the following reaction mechanism is proposed.



A photoreaction of 2,3-dimethyl-2-butene in oxygen matrices was reported by HASHIMOTO and AKIMOTO [14], who reported that oxidation of 2,3-dimethyl-2-butene occurred by irradiation at wavelengths shorter than 520 nm. They observed the IR spectrum of a reaction intermediate, tetramethyl-1,2,3,4-tetraoxane, and assumed a charge transfer complex between $O_2$ and 2,3-dimethyl-2-butene, the electronic absorption spectrum of which was also observed. In the present system, involvement of a charge transfer complex of 2,3-dimethyl-2-butene with $NO_2$ can be ruled out because the IR spectrum of the alkene–$NO_2$–Ar matrix was the same as the superposition of 2,3-dimethyl-2-butene–Ar and $NO_2$–Ar spectra. No new band for the complex could be found. Alkene–$NO_2$ charge transfer absorption bands in solid argon have been reported previously and lie in the UV spectral region [6].

### *Determination of rate constants*

In order to determine the reaction rate constants from the intensity changes of the IR bands at 1717 $cm^{-1}$ for 3,3-dimethyl-2-butanone, 1206 $cm^{-1}$ for tetramethyloxirane and 744 $cm^{-1}$ for the nitrite radical, shown in Fig. 6, we assumed the following reaction scheme by analogy with other alkene + $NO_2$ photoreactions in our previous works [1–10]:



where $k_1$, $k_{2B}$ and $k_{2O}$ denote rate constants. The rate equations are easily solved [15], and the result is

$$A^N = A^R(\varepsilon^N/\varepsilon^R)(k_1/(k_2 - k_1))[\exp(-k_1 t) - \exp(-k_2)] \quad (1)$$

$$A^B = A^R(\varepsilon^B/\varepsilon^R)(k_{2B}/k_2)[1 + (k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t))/(k_1 - k_2)] \quad (2)$$

$$A^O = A^R(\varepsilon^O/\varepsilon^R)(k_{2O}/k_2)[1 + (k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t))/(k_1 - k_2)], \quad (3)$$

where $k_2 = k_{2B} + k_{2O}$. $A^R$, $A^N$, $A^B$ and $A^O$ are the absorbance of the reactant, nitrite radical, 3,3-dimethyl-2-butanone and tetramethyloxirane. $\varepsilon^R$, $\varepsilon^N$, $\varepsilon^B$ and $\varepsilon^O$ are the absorption coefficients of the corresponding species. From Eqns (2) and (3), the ratio $A^B$ and $A^O$ is simply expressed as

$$A^B/A^O = (\varepsilon^B/\varepsilon^O)(k_{2B}/k_{2O}). \quad (4)$$

The experimental values obtained for $A^B/A^O$ are essentially constant and independent of laser wavelength, as shown in Fig. 6. The calculated values were 3.26 ± 0.15 for 635 nm, 3.39 ± 0.15 for 615 nm and 3.40 ± 0.15 for 595 nm irradiation. Since these values stay constant within experimental error, it is reasonable to assume that the branching ratio of the final products, 3,3-dimethyl-2-butanone and tetramethyloxirane, is constant: the average value of $A^{1717}/A^{1206}$ is 3.35. Since the ratio of absorption coefficients, $\varepsilon^{1717}/\varepsilon^{1206}$, is estimated to be around six from the IR spectra of the authentic samples, the ratio of $k_{2B}$ and $k_{2O}$ is calculated to be 0.558 by dividing 3.35 by six, according to Eqn (4).

In order to obtain the rate constants $k_1$ and $k_2$, we must estimate the absorption coefficients of the IR bands at 1717, 1206 and 744 cm$^{-1}$. From Fig. 4, one is able to estimate $A^{1717}/A^{1206}/A^{744}$ to be 17 : 5 : 39. By using this experimental value and the ratio of the absorption coefficients, $\varepsilon^{1717}/\varepsilon^{1206} = 6$, the ratio of the absorption coefficients, is estimated to be $\varepsilon^{1717}/\varepsilon^{1206}/\varepsilon^{744} = 6:1:5$. This is derived from $A^{1717}/\varepsilon^{1717} + A^{1206}/\varepsilon^{1206} = A^{744}/\varepsilon^{744}$ if we further assume that the one-photon generation of the final products is negligible (i.e. both oxirane and ketone are generated from nitrite radical by secondary photolysis). Replacing $A^{R}(\varepsilon^{N}/\varepsilon^{R})$ by $r$, Eqns (1)–(3) can be written as

$$A^{N} = r(k_1/(k_2 - k_1))[\exp(-k_1 t) - \exp(-k_2 t)] \tag{5}$$

$$\begin{aligned} A^{B} &= r(\varepsilon^{B}/\varepsilon^{R})(k_{2B}/k_2)[1 + (k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t))/(k_1 - k_2)] \\ &= r(6/5)(0.558/1.558)[1 + (k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t))/(k_1 - k_2)] \\ &= r(0.430)[1 + (k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t))/(k_1 - k_2)] \end{aligned} \tag{6}$$

$$\begin{aligned} A^{O} &= r(\varepsilon^{O}/\varepsilon^{R})(k_{2O}/k_2)[1 + (k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t))/(k_1 - k_2)] \\ &= r(1/5)(1/1.558)[1 + (k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t))/(k_1 - k_2)] \\ &= (1/3.35)A^{B}. \end{aligned} \tag{7}$$

We determined the three parameters $r$, $k_1$ and $k_2$ by use of the absorbance changes of nitrite radical and 3,3-dimethyl-2-butanone by least-square fitting. The rate constants so obtained, $k_1$ and $k_2$, are shown in Table 4. The rate constants $k_{2B}$ and $k_{2O}$ were calculated from $k_2(= k_{2B} + k_{2O})$ and $k_{2B}/k_{2O}(= 0.558)$. The solid lines drawn in Fig. 6 represent the calculated curves. All rate constants increase as the photolysis light shifts to shorter wavelengths. Note that the rate constant $k_2$ increases much more rapidly than $k_1$.

### *Comparison of rate constants*

The rate constants depend on the irradiation wavelength and laser power. We calculated the relative photon density from the measured power and wavelength in order to normalize the rate constants, as done previously in the case of other alkenes [1–10]. These normalized rate constants are proportional to the product of reaction quantum yield and extinction coefficient of $NO_2$ at the corresponding wavelength [1]. In Figs 7 and 8, we compare the normalized rate constants $k_1 + k_3$ and $k_2$ for $NO_2$ photoreactions with alkenes. According to Scheme 2, $k_1 + k_3$ and $k_2$ represent the rate constants for photoreaction of alkene–$NO_2$ pairs and secondary photolysis of trapped alkyl nitrite radical, respectively. It is found in Fig. 7 that the magnitudes of $k_1 + k_3$ become larger with increasing number of methyl groups at the C=C bond: ethylene < 2-butenes, methylpropene < 2,3-dimethyl-2-butene. The threshold of photoreaction also shifts to longer wavelength with increasing number of methyl groups: ethylene (555 nm) < 2-butenes, methylpropene (620 nm) < 2,3-dimethyl-2-butene (650 nm).

As shown in Fig. 8, the threshold of secondary photolysis of the alkyl nitrite radical shifts to longer wavelengths with increasing number of methyl groups. The steep increase of $k_2$ may either reflect a rapid increase of the absorption cross-section of the nitrite radical, the photodissociation quantum efficiency, or both. In the case of *cis*- and *trans*-2-butene, these alkyl nitrite radical visible absorptions have recently been reported [6], and

Table 4. Photolysis wavelength dependence of first-order rate constants

| $\lambda$(nm) | $k_1$(h$^{-1}$) | $k_2$(h$^{-1}$) | $k_{2B}$(h$^{-1}$) | $k_{2O}$(h$^{-1}$) |
|---|---|---|---|---|
| 635 | 0.28 ± 0.13 | 0.79 ± 0.09 | 0.28† | 0.51† |
| 615 | 0.57 ± 0.14 | 1.87 ± 0.14 | 0.67† | 1.20† |
| 595 | 0.94 ± 0.14 | 4.82 ± 0.38 | 1.72† | 3.10† |

† Obtained by the use of two relationships, $k_2 = k_{2B} + k_{2O}$ and $k_{2B}/k_{2O} = 0.5583$ (see text).

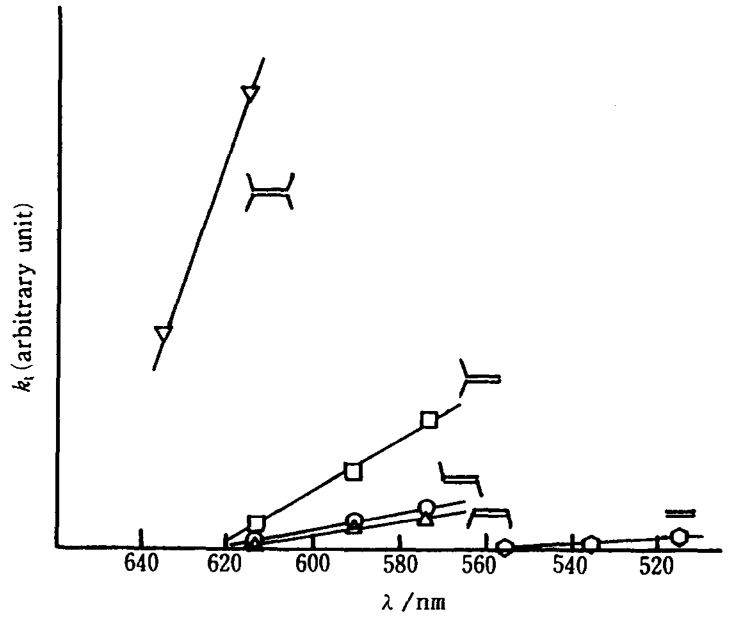


Fig. 7. A comparison of normalized rate constants, $k_1 + k_3$, of photoreactions of $NO_2$ with alkenes. Symbols ○, △, O, □ and ▽ represent ethylene, *cis*-2-butene, *trans*-2-butene, methylpropene and 2,3-dimethyl-2-butene, respectively. The obtained rate constants were normalized with respect to the laser photon density calculated from laser wavelength and laser power.

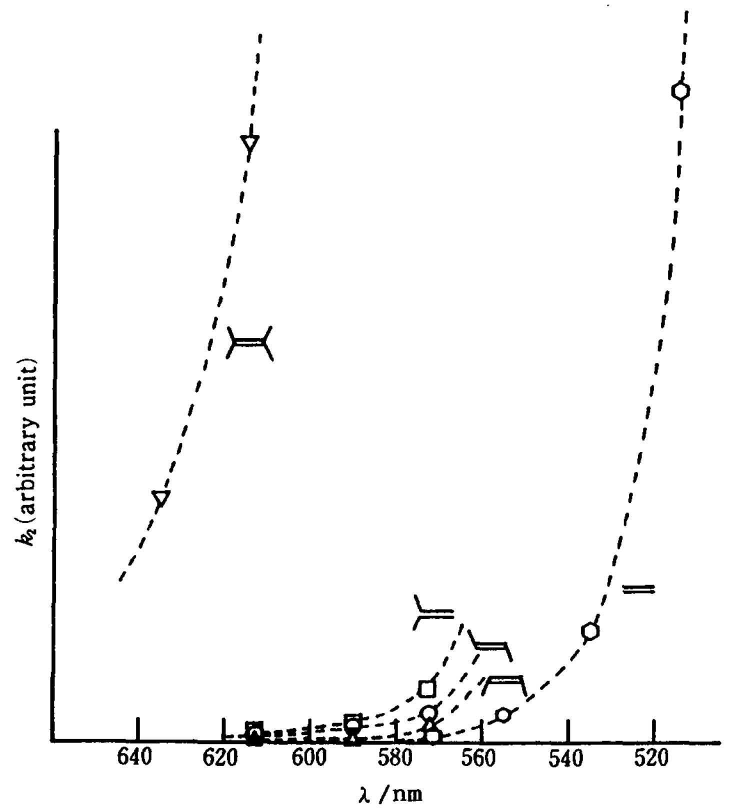


Fig. 8. A comparison of normalized rate constants, $k_2$, of photoreactions of $NO_2$ with alkenes. symbols ○, △, O, □ and ▽ represent ethylene, *cis*-2-butene, *trans*-2-butene, methylpropene and 2,3-dimethyl-2-butene, respectively. The obtained rate constants were normalized with respect to the laser photon density calculated from laser wavelength and laser power.

it was found that the dissociation quantum yield increases significantly towards higher photolysis photon energies. In any event, the data presented here show that the threshold of the electronic absorption shifts to longer wavelength with increasing number of methyl groups.

## CONCLUSIONS

Red light-induced photoreaction between 2,3-dimethyl-2-butene and $NO_2$ in a low-temperature matrix was studied by IR spectroscopy. It was found that the photoreaction occurred by irradiation at substantially longer wavelengths than in the case of smaller alkenes. The IR spectrum of a reaction intermediate, 2,3-dimethyl-2-butyl nitrite radical, was observed. The frequencies of N=O stretching and O–N stretching modes of this species are shifted to the red compared with smaller alkyl nitrite radicals. Kinetic analysis of IR absorbance growth revealed that the final oxidation products tetramethyloxirane and 3,3-dimethyl-2-butanone (pinacolone) emerge from secondary photolysis of the trapped alkyl nitrite radical intermediate. The rate constants for reaction of 2,3-dimethyl-2-butene–$NO_2$ pairs and for secondary photolysis of the nitrite radical were compared with those for photoreactions between $NO_2$ and smaller alkenes. It was concluded that the threshold for reaction of ethylene and its methyl-substituted derivatives with $NO_2$ in a low-temperature argon matrix shifts toward longer wavelengths as the number of methyl groups is increased.

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