PHOTOÖXIDATION OF BUTENE-1 AND ISOBUTENE BY NITROGEN DIOXIDE[1]

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ABSTRACT

Reactions of oxygen atoms, produced by photolysis of nitrogen dioxide at 3660 Å, with butene-1 and isobutene have been studied at room temperature. In the case of butene-1, α-butene oxide and *n*-butanal have been identified as the major products, and methyl ethyl ketone, propanal, acetaldehyde, and ethyl nitrate as minor products. With isobutene, isobutanal was recovered as the major product and acetone, methyl ethyl ketone, methyl nitrate, and nitromethane as minor products. The absence of isobutene oxide in the recovered products from the isobutene reaction is due to its rapid reaction with nitrogen dioxide.

The following values were obtained for the relative reaction rates of oxygen atoms with nitrogen dioxide (k_2), butene-1 (k_{4a}), and isobutene (k_{4b}): $k_2/k_{4a} = 1.9$, $k_2/k_{4b} = 0.34$, $k_{4b}/k_{4a} = 5.5$.

INTRODUCTION

The photochemical reaction between nitrogen dioxide and olefins has been studied especially from the point of view of its relation to "smog" formation in polluted atmosphere (1), but little information has been obtained about the reaction mechanism and the type of products formed. In a previous communication (2) the authors have reported a long wave length threshold for the photochemical reaction between nitrogen dioxide and butene-1. The reaction occurs at 4047 Å and shorter wave lengths, with the formation of α-butene oxide and *n*-butanal as the main products, but does not occur at 4358 Å and longer wave lengths. It has, therefore, been assumed that even at 4047 Å nitrogen dioxide decomposes and forms free oxygen atoms in their ground electronic state,

$$NO_2 + h\nu = NO + O(^3P). \tag{1}$$

The photolysis of nitrogen dioxide itself has been extensively investigated (3). In the absence of foreign gases reaction (1) is followed by

$$O + NO_2 = NO + O_2. \tag{2}$$

When an olefin is added, nitrogen dioxide and the olefin compete for the oxygen atoms formed in reaction (1).

Reactions of oxygen atoms, produced by the mercury-photosensitized decomposition of nitrous oxide, have been studied in this laboratory for some time. In the case of olefins (4), studied at pressures between about 50 and 600 mm., oxygen atoms add to the olefinic double bond, and isomeric epoxides, aldehydes, and ketones are formed as the main products when the olefins consist of more than three carbon atoms. Propylene and ethylene require a collisional stabilization of the addition products formed.

In this paper, results of a study of the photochemical reaction of nitrogen dioxide with butene-1 and isobutene at 3660 Å are reported. At this wave length oxygen atoms produced in reaction (1) are in their ground state.

EXPERIMENTAL

Nitrogen dioxide was obtained from Matheson Co., Inc., and was further purified by repeated bulb-to-bulb distillation *in vacuo* at Dry Ice temperature. The middle third was

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retained and stored at liquid nitrogen temperature. The color of the solid was pure white. Butene-1 and isobutene were Phillips reagent grade products, and were purified by repeated bulb-to-bulb distillation *in vacuo.* Nitrogen gas was supplied by Linde Air Products Co., and was used without further purification.

Because of rapid reaction of nitrogen dioxide with mercury it was necessary to use a mercury-free apparatus. Stopcocks were lubricated with Myvacene-S (Dow Corning) which was not attacked by nitrogen dioxide. Pressures were measured by means of a Bourdon gauge and the compensating pressures were read on a mercury or a silicon oil manometer. The reaction cell consisted of a 300 ml. quartz cylindrical vessel with an all-glass circulating pump supported on teflon bearings and a trap for condensing the reactants attached to it. The light from a medium-pressure mercury arc (Hanovia S 500) was used with Corning glass filter 7-60 so that essentially only the monochromatic light of 3660 Å entered the reaction cell. The cell and the attachments were screened from the diffuse light in the room.

The products formed were fractionated on a LeRoy still (5). Unreacted butene was pumped off at −120° C. and the remainder was transferred into a sampling tube containing a few drops of mercury to remove the unreacted nitrogen dioxide. This tube had been previously evacuated on a second, mercury-containing, high-vacuum apparatus. After the completion of the reaction between nitrogen dioxide and mercury, the tube was evacuated again at liquid nitrogen temperature. Subsequently the products were analyzed by gas–liquid chromatography (GLC) using a 7 ft. dinonyl-phthalate-on-glass-beads column (6, 4) and helium as the carrier gas. To confirm the identity of the compounds separated by GLC, use was made of infrared and mass spectroscopy. The quantitative estimate of the products was based on GLC peak areas.

RESULTS AND DISCUSSION

Thermal Reaction

Nitrogen dioxide attacks olefins thermally and forms addition products (7). Under the conditions employed in this work, however, the thermal reaction was much slower than the photochemical reaction. Moreover, it was found that no products formed in the thermal reaction, with the exception of nitric oxide, were recorded by the GLC. The thermal reaction between nitrogen dioxide and butene was, therefore, ignored in the present work.

Photochemical Reaction

The amounts of the main products formed* at various irradiation times and constant light intensity in the reaction of 3 mm. nitrogen dioxide with 3 mm. and 30 mm. butene-1 are shown in Fig. 1(*a*), and with 3 mm. isobutene in Fig. 1(*b*). The products formed increase almost linearly with the irradiation time up to 30 minutes and the primary processes of these reactions were subsequently studied within this time interval.

The main products formed in the case of butene-1 are the same as found previously for this reaction with the use of O atoms produced by mercury-photosensitized decomposition of nitrous oxide (4). In the case of isobutene, however, isobutene oxide, one of the two main products of the reaction (4), was usually not observed (Fig. 1*b*). This was shown to be due to its rapid reaction with excess nitrogen dioxide. A sample of isobutene oxide was kindly supplied by Dr. A. M. Eastham of these laboratories and its removal

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**In the presence of large excess of unreacted NO_2 no attempt could be made to analyze for NO, formed in reactions (1) and (2), and for O_2, formed in reaction (2). A knowledge of the amounts of these products, however, is not essential for the present study.*

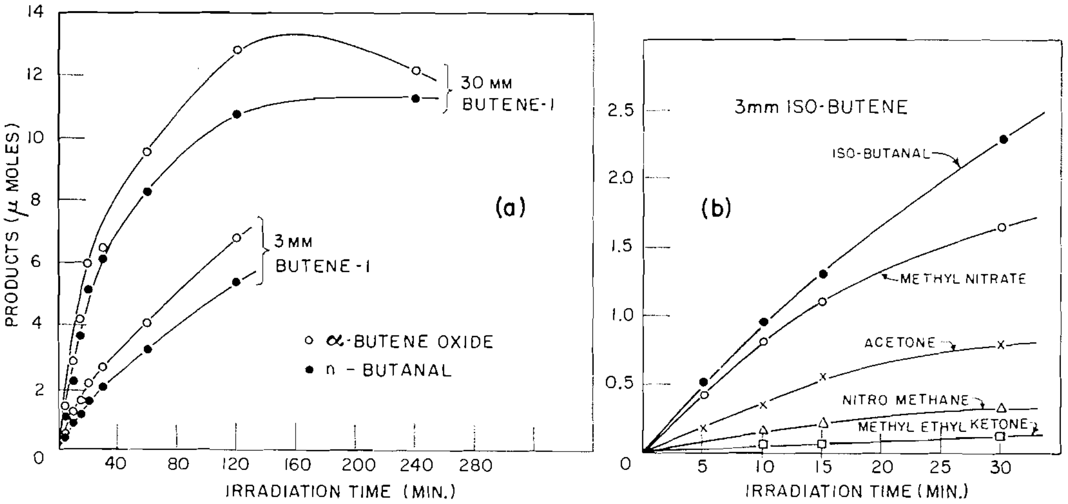


FIG. 1. Yield of the principal products as a function of irradiation time in the photoöxidation of (*a*) butene-1 and (*b*) isobutene.

in the presence of nitrogen dioxide and under conditions employed in the present experiments was demonstrated. The much greater reactivity of isobutene oxide relative to that of the 1,2-epoxides of *n*-olefins has been observed before (8).

Typical chromatograms of the reaction products are shown in Fig. 2. In the case of butene-1 (Fig. 2, A), the main products are α-butene oxide and *n*-butanal, and the minor products are methyl ethyl ketone, propanal, acetaldehyde, ethyl nitrate, and two unidentified compounds (compounds *a* and *b*). In the case of isobutene (Fig. 2, B) isobutanal appears as the only major product since isobutene oxide is removed by excess

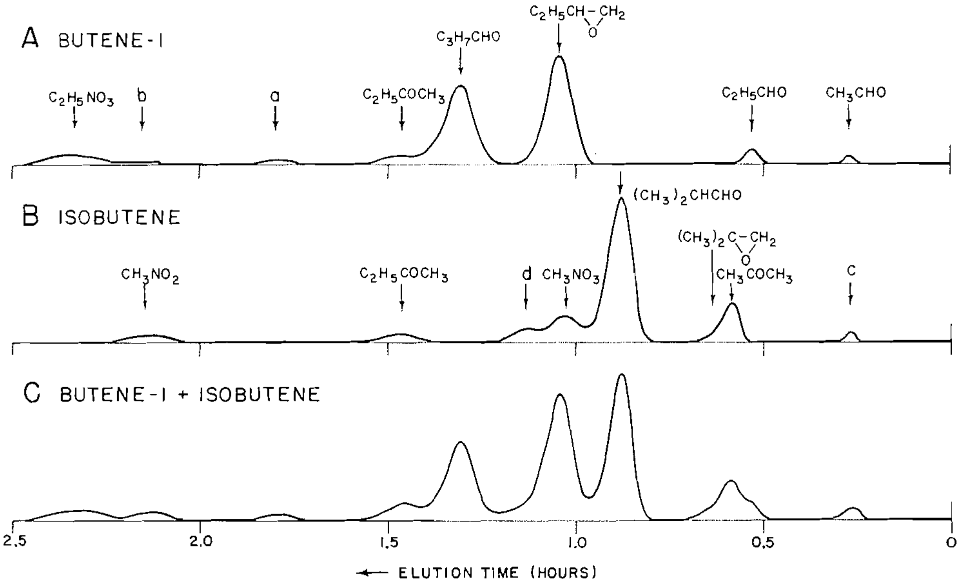


FIG. 2. Typical GLC peaks: A, photoöxidation of butene-1; B, photoöxidation of isobutene; and C, photoöxidation of mixtures of butene-1 and isobutene. (Column temperature 25° C.)

nitrogen dioxide; acetone, methyl nitrate, methyl ethyl ketone, nitromethane, and two unknown compounds (compounds *c* and *d*) are minor products. It was shown that these minor products were not formed in the thermal reaction of isobutene oxide and nitrogen dioxide.

Fig. 2, C shows the chromatogram of the products of a simultaneous photoöxidation of butene-1 and isobutene. No new products are observed but only those obtained in the reactions of the two butenes separately. This is in agreement with the previous conclusion (4) that the principal reactions under consideration do not involve a free-radical mechanism.

Effect of Pressure

Figs. 3(*a*) and 3(*b*) show the effect of pressure on the photochemical reactions of nitrogen dioxide with butene-1 and isobutene, respectively, at a constant irradiation time of 30 minutes. In both cases 1 mm. each of nitrogen dioxide and the olefin and various amounts of nitrogen were used. There is a pressure effect of the type observed previously (4) for propylene but in the present case it is confined to the pressures below about 30 mm. The lifetimes of the "hot" addition products formed appear to be an order of magnitude longer

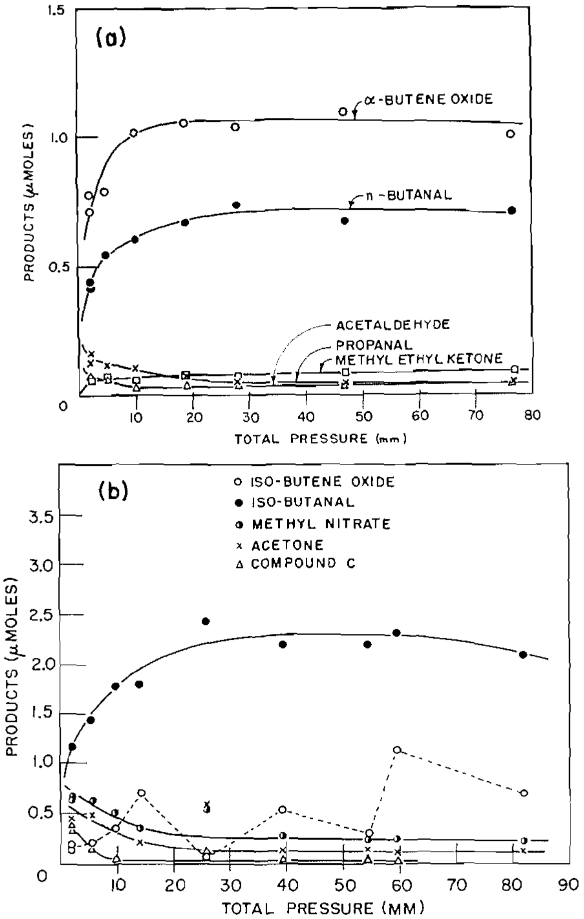


FIG. 3. Pressure effects in the photoöxidation of (*a*) butene-1 and (*b*) isobutene.

than in the case of propylene and the collisional stabilization, therefore, takes place at much smaller pressures. At pressures higher than about 70 mm. the rates of formation of the major products seem to show a tendency to decrease again. This is probably due to the additional consumption of oxygen atoms in the three-body reaction

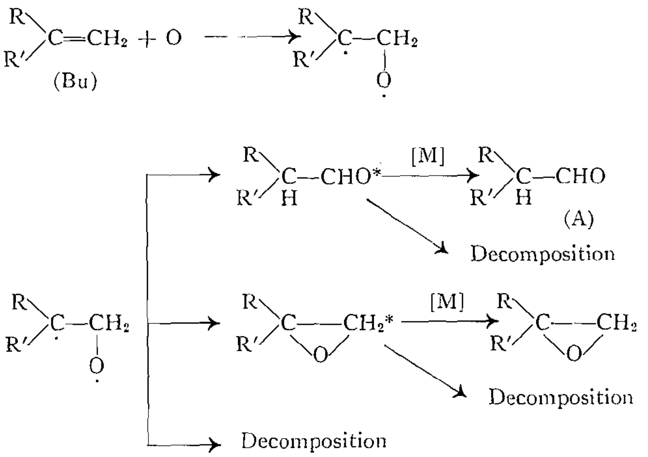
$$O + NO_2 + M = NO_3 + M. \qquad (3)$$

No analogous decline was observed when O atoms were generated by the mercury-photosensitized decomposition of nitrous oxide (4).

In the case of butene-1 throughout the investigated pressure range the ratio of *n*-butanal to α-butene oxide was 0.40±0.02 to 0.60±0.02. In the case of isobutene only small and irregular quantities of isobutene oxide were recovered, for reasons already discussed. In the nitrous oxide work (4) the respective ratios of the aldehyde to the epoxide formed for the case of butene-1 and isobutene were 0.43 to 0.57 and 0.42 to 0.58.

Relative Reaction Rates of Oxygen Atoms with Nitrogen Dioxide, Butene-1, and Isobutene

Oxygen atoms are believed (4) to react with terminal monoölefins according to the following scheme:



(4)

(5)

(6)

(7)

(8)

(9)

At a pressure of, for example, 40 to 50 mm. reactions (6) and (8) need not be considered. At small conversions and on applying the usual steady-state treatment to the remaining reactions and writing Bu for the butene and A for the aldehyde formed in reaction (5), the following relationship is obtained:

$$[1] \qquad \frac{\alpha\phi I[NO_2]}{R_A} = 1+\frac{k_2}{k_4}\frac{[NO_2]}{[Bu]}\left(1+\frac{k_3}{k_2}[M]\right),$$

where $\phi I[NO_2]$ is the rate of light absorption by nitrogen dioxide (at small I and $[NO_2]$), R_A the rate of formation of the aldehyde A produced in reaction (5), and α the ratio of molecules of A formed to the number of oxygen atoms consumed in reaction (4). At constant $[NO_2]$, $[M]$, irradiation time, and light intensity (I) a plot of reciprocal GLC peak areas of the compound A against $[NO_2]/[Bu]$ is linear. The slope-to-intercept ratio is

$$[2] \qquad m = \frac{k_2}{k_4}\left(1+\frac{k_3}{k_2}[M]\right).$$

Also

$$[3] \qquad k_{4a}/k_{4b} = m_b/m_a,$$

where the suffixes *a* and *b* refer to the butene-1 and the isobutene reaction, respectively.

The composition of the main products recovered after 15 minutes irradiation of NO_2–butene-1 mixtures at a total pressure of 50 mm. and at constant NO_2 but variable $[NO_2]/[Bu]$ ratios is shown in Table I, and for the NO_2–isobutene mixtures at a total pressure of 40 mm. in Table II.

TABLE I

YIELD OF THE PRINCIPAL PRODUCTS IN THE PHOTOÖXIDATION OF BUTENE-1 AS A FUNCTION OF THE $[NO_2]/[Bu\text{-}1]$ RATIO

(Irradiation time 15 min.)

Bu-1, mm.	NO_2, mm.	N_2, mm.	$[NO_2]/[Bu\text{-}1]$	GLC peak areas (cm.^{2})				
				n-BuA	α-BuO	PrA	MEK	AcA
28.9	3.1	11.3	0.11	12.9	16.2	0.3	1.5	0.3
19.4	3.1	27.6	0.16	12.6	16.0	0.5	1.0	0.4
12.9	3.1	36.7	0.24	11.2	15.9	0.6	1.3	0.4
9.2	3.1	37.0	0.34	10.8	14.3	0.5	1.1	0.5
7.1	3.1	39.2	0.44	8.4	11.9	0.5	1.0	0.5
6.0	3.1	40.7	0.52	8.1	11.1	0.4	0.8	0.4
5.0	3.1	41.3	0.62	7.4	9.4	0.5	0.8	0.4
4.5	3.1	42.4	0.69	6.0	8.1	0.4	0.8	0.3
3.9	3.1	43.2	0.79	6.6	9.1	0.4	0.6	0.3
3.3	3.0	43.3	0.91	5.9	6.2	n.d.	0.5	0.5
3.0	3.1	44.0	1.03	5.2	7.5	0.3	0.5	0.3

Bu-1 = *butene; n*-BuA = *n-butanal;* α-BuO = *α-butene oxide;* PrA = *propanal;* MEK = *methyl ethyl ketone;* AcA = *acetaldehyde; n.d. = not determined.*

TABLE II

YIELD OF THE PRINCIPAL PRODUCTS IN THE PHOTOÖXIDATION OF ISOBUTENE AS A FUNCTION OF THE $[NO_2]/[\text{ISOBUTENE}]$ RATIO

(Irradiation time 15 min.)

i-Bu, mm.	NO_2, mm.	N_2, mm.	$\frac{[NO_2]}{[i\text{-}Bu]}$	GLC peak areas (cm.^{2})							
				i-BuA	CH_3NO_3	Acetone	*i*-BuO	MEK	CH_3NO_2	Cpd. *c*	Cpd. *d*
29.2	3.1	6.7	0.11	19.2	2.5	1.7	0	0.8	1.8	0.1	1.5
9.1	3.1	26.0	0.34	17.9	2.2	2.7	0	0.8	1.0	0.2	1.4
4.8	3.1	28.0	0.65	16.2	n.d.	2.6	n.d.	n.d.	n.d.	n.d.	n.d.
3.0	3.1	33.3	1.03	12.8	2.4	2.4	0	0.3	1.0	0.3	1.4
2.0	3.1	34.3	1.6	13.4	2.5	2.5	0	0.5	0.8	0.3	1.0
1.6	3.1	34.4	2.0	11.8	2.6	1.8	0	0.4	1.0	0.3	1.2
1.5	3.1	35.6	2.1	11.7	2.1	2.0	0	0.6	0.8	0.3	1.5
1.2	3.1	38.2	2.6	11.0	1.9	1.5	0.1	0.4	0.7	0.4	1.1
0.98	3.1	38.0	3.2	9.4	1.6	1.2	0.6	0.3	1.0	0.3	1.0
0.85	3.1	39.1	3.7	8.0	1.4	1.2	0.2	0.3	0.7	0.3	1.0
0.75	3.1	39.6	4.2	7.7	2.1	1.9	0	0.2	0.5	0.2	0.7

i-Bu = *isobutene; i*-BuA = *isobutanal; i*-BuO = *isobutene oxide;* MEK = *methyl ethyl ketone; n.d. = not determined.*

The reciprocal peak areas of *n*-butanal and isobutanal, respectively, are plotted against $[NO_2]/[Bu]$ in Figs. 4(*a*) and 4(*b*). There is an appreciable scatter of experimental values and the least mean squares treatment gives $m_a = 2.1$ and $m_b = 0.38$. These quantities are approximately equal to k_2/k_{4a} and k_2/k_{4b}, respectively, since at pressures of 40 to 50 mm. the expression in the bracket in Eq. [2] does not differ much from unity. According to Ford and Endow (9), $k_3[M]/k_2 = 47.6$ [M] (where [M] is in mole/l.) so that the corrected values are

$$k_2/k_{4a} = 1.9, \quad \text{and} \quad k_2/k_{4b} = 0.34.$$

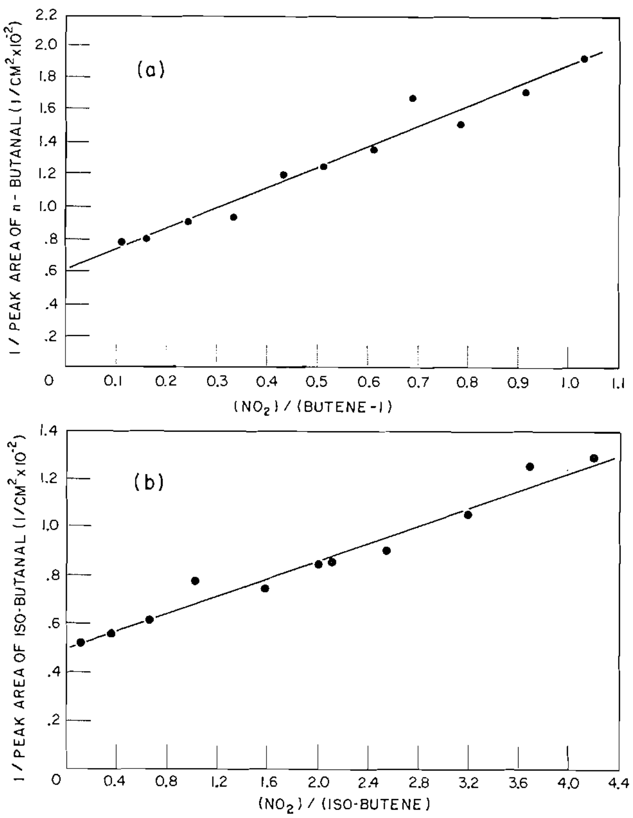


FIG. 4. (*a*) Reciprocal GLC peak areas of *n*-butanal as a function of the $[NO_2]/[\text{butene-1}]$ ratio (*b*) Reciprocal MLC peak areas of isobutanal as a function of the $[NO_2]/[\text{isobutene}]$ ratio.

The ratio of the rate constants of the reactions of oxygen atoms with butene-1 and isobutene is, therefore,

$$k_{4b}/k_{4a} = 5.5.$$

By photolyzing nitrogen dioxide in the presence of mixtures of butene-1 and isobutene, this ratio of the rate constants can be also evaluated from the relationship

$$[4] \qquad \frac{k_{4b}}{k_{4a}} = \frac{[R_A]_b\,\alpha_a\,[\text{butene-1}]}{[R_A]_a\,\alpha_b\,[\text{isobutene}]}.$$

Table III shows the amounts of *n*-butanal and isobutanal formed with various mixtures of butene-1 and isobutene. The two aldehydes have essentially the same molar GLC responses, as is shown in Fig. 5. Since it has also been found before (4) that $\alpha_a/\alpha_b \approx 1$, the relative rate constant in Eq. [4] is obtained simply by multiplying the ratio of the GLC peak areas of the two aldehydes by the inverse ratio of the concentrations of the butenes. The values obtained are given in the last column of Table III. The mean value of about 5.8 agrees well with the above value of 5.5. There is, however, a considerable scatter from the mean value and perhaps also a systematic drift with the ratio of the two olefins: a decrease with decreasing isobutene to butene-1 ratio extrapolating to a limit of about 4.5 as the amount of isobutene tends to zero. In view of this and of the

TABLE III

YIELD OF ALDEHYDES IN THE PHOTOÖXIDATION OF MIXTURES OF BUTENE-1 AND ISOBUTENE

NO_2, mm.	*i*-Bu, mm.	Bu-1, mm.	N_2, mm.	Irradiation time, min.	GLC peak areas (cm.^{2})		k_{4b}/k_{4a}
					n-BuA	*i*-BuA	
3.1	0.98	3.95	31.0	15	6.8	10.1	5.9
3.2	0.81	4.97	32.3	15	7.9	6.9	5.4
3.1	1.26	3.48	31.8	15	3.9	9.1	6.4
6.2	1.00	4.10	32.1	10	6.4	9.1	5.7
3.1	0.99	4.02	31.6	15	4.8	6.8	5.8
						Average	5.8

i-Bu = *isobutene;* Bu-1 = *butene-1;* *n*-BuA = *n-butanal;* *i*-BuA = *isobutanal.*

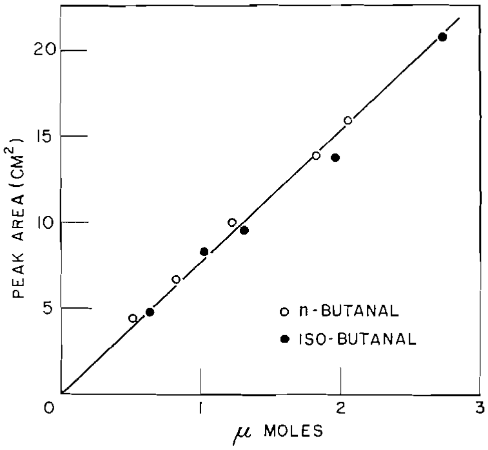


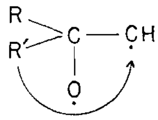
FIG. 5. GLC molar responses of *n*-butanal and isobutanal.

scatter of points in the plots in Figs. 4(*a*) and 4(*b*), it is felt that there is probably an experimental uncertainty of the order of 20 to 30 per cent in the relative rate constants determined in the present work. Previously (4) a value of 4.2 was obtained for k_{4b}/k_{4a}, which within the estimated experimental uncertainties agrees with the present value.

Formation of Minor Products

The complexity of the reactions and the incomplete analytical information preclude a detailed explanation of the method of formation of minor products.

Small amounts of methyl ethyl ketone were found in the case of both butene-1 and isobutene. The formation of this compound has been explained before (4) by addition of a small amount of oxygen atoms to the "more-substituted" carbon atom in the two butenes followed by migration of H or CH_3.



This migration is probably largely intramolecular, although the formation of nitromethane in the isobutene system suggests the presence of some free methyl radicals.

Most of the minor products increase at lower pressures, as is shown in Figs. 3(*a*) and

3(*b*). This is in agreement with an increasing importance of reactions (6) and (8) at lower pressures. However, even at higher pressures certain amounts of minor products are still formed, suggesting also the occurrence of some pressure-independent decomposition (reaction (9)).

Finally, it should be mentioned that under certain conditions in the presence of molecular oxygen propanal and acetone are formed as major products in the reactions of butene-1 and isobutene, respectively, besides the C_4 epoxides and aldehydes which are normally the only major products in these reactions. While these effects require further investigation, it is possible that oxygen produced in reaction (2) may contribute to some extent to the formation of propanal and acetone even when only nitrogen is used as diluent.

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