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Furan Ring Formation in OH-initiated Photooxidation of 1,3-Butadiene and *cis*-1,3-Pentadiene

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Reactions of hydroxyl radicals with 1,3-butadiene and *cis*-1,3-pentadiene in the presence of oxygen were studied in the gas phase. Two OH radical sources were employed; photolysis of H_2O_2 at 254 nm and photolysis of methyl nitrite at 360 nm. In the reaction system for 1,3-butadiene, furan was detected besides acrylaldehyde and in the *cis*-1,3-pentadiene system, 2-methylfuran was detected besides acetaldehyde, acrylaldehyde, and crotonaldehyde by gas chromatographic analysis. Approximate yields of furan and 2-methylfuran were 5.3—6.7% and 6.7—8.4%, respectively, which were sensitive to the conditioning of the surface of reactor but insensitive to hydroxyl radical sources, the surface material of reaction vessel or the surface to volume ratio of reactors. The yields of aldehydes were also measured. Isotopic labeling experiment with $^{18}O_2$ by use of mass spectrometry indicated that abstraction of vinyl-hydrogen from 1,3-butadiene and *cis*-1,3-pentadiene occurred about 3% of the time. Photooxidation of 2,5-dihydrofuran initiated with ·OH radicals was also discussed to explain the increase of furan in the dark after the irradiation.

Atmospheric reactions of ·OH radicals with simple monoolefins are understood to be initiated mainly by ·OH radical addition to double-bond and partly by hydrogen abstraction at allylic position.[1] When a general olefin $R_1R_2C=CR_3R_4$ is photooxidized in NO_x-polluted atmosphere, major expected products are $R_1R_2C=O$ and $R_3R_4C=O$. It is interesting to know whether the general rule is applicable to diolefins. Environmental chamber studies[2,3] have shown that the major initial products of NO_x-air photooxidation of 1,3-butadiene were formaldehyde and acrylaldehyde. *cis*-1,3-Pentadiene is expected analogously to produce formaldehyde, acetaldehyde, acrylaldehyde, and crotonaldehyde in the similar photooxidation process. However, in our previous study[4] on the determination of relative rate constants for the reactions of diolefins with ·OH radicals by photolyzing H_2O_2 in the presence of oxygen and pairs of diolefins, it was found that furan was formed in the reaction of ·OH with 1,3-butadiene and that 2-methylfuran was formed in *cis*-1,3-pentadiene system, in addition to the expected aldehydes. In order to determine the yield of furans and to make an assumption on the mechanism for furan ring formation in the photooxidation of the conjugated diolefins, we carried out several experiments on the system and proposed a mechanism involving abstraction of vinyl-hydrogen by ·OH from conjugated diolefins.

Experimental

Two ·OH radical sources were employed separately; photolysis of hydrogen peroxide (H_2O_2, 90 %) at 254 nm and methyl nitrite (CH_3ONO) at 360 nm. Hydrogen peroxide was used for runs to examine the dependence of the product yield on the initial concentrations of reactants and wall effect. First, 1 Torr (1 Torr=133 Pa) of H_2O_2 (90%) was introduced in a quartz cylindrical reaction cell which was 15 cm in length and 4 cm in diameter (surface to volume ratio, $S/V,=1.1$ cm^{-1}): this cell was named reactor A for later discussion. Then, diluted 1,3-butadiene or *cis*-1,3-pentadiene in O_2 was added by measuring the pressure with MKS Baratron. Oxygen or nitrogen gas was filled into the cell to pressurize the mixture up to 760 Torr. After allowing the mixture to stand for about 10 min, the cell was irradiated with two 15 W germicide lamps (National GL-15, 254 nm). Products and reactants for 1,3-butadiene system were analyzed by gas chromatography with flame ionization detector by using 1-m glass column of Porapak T operated at 145 °C. For the reaction system of *cis*-1,3-pentadiene, 1-m stainless steel column of Porapak Q was employed. Products of several runs were trapped in a tube filled with small glass beads immersed in liquid oxygen and the solidified fraction was vaporized and, then, analyzed by use of a gas chromatograph-mass spectrometer (LKB 9000) with the same kind of column used for each reaction system. Further identification was made with infrared spectrometer for the effluents from thermal conductivity detector (TCD) corresponding to furan and 2-methylfuran collected repeatedly in the trap cooled with liquid nitrogen by monitoring TCD signal. Carrier gas was helium.

The other ·OH radical source, CH_3ONO, was used for the experiments to carry out the reactions of ·OH with the diolefins in the absence of H_2O_2 and in the presence of NO_x, and also to examine wall effect on the reaction. Atkinson *et al.*[5,6] have shown that CH_3ONO is a good source *via* Reactions 1 to 3.

$$CH_3ONO + h\nu(360\,\text{nm}) \rightarrow CH_3O + NO \tag{1}$$

$$CH_3O + O_2 \rightarrow HO_2 + CH_2O \tag{2}$$

$$HO_2 + NO \rightarrow HO + NO_2 \tag{3}$$

Methyl nitrite was prepared from the reaction of methanol, sodium nitrite and sulfuric acid, according to Atkinson *et al.*[5,6] Crude CH_3ONO was vacuum distilled in a greaseless high-vacuum system and stored under vacuum at 77 K in the dark. Procedure for preparing the reaction mixture was similar to the method for the H_2O_2 system. The irradiation source was black light blue fluorescence lamps (Toshiba BLB, $\lambda_{max}=360$ nm).

Four more reactors were used besides reactor A, in order to check wall effect: reactor B was 2 l-quartz cylindrical cell ($S/V=0.55\,cm^{-1}$); reactor C was 188 ml-Pyrex cylindrical cell ($S/V=1.2\,cm^{-1}$); reactor D was 94 ml-Pyrex long tube cell ($S/V=4.0\,cm^{-1}$); reactor E consisted of 25.2 l-Pyrex photochemical chamber and 7.57 l-stainless steel optical absorption cell of UV-VIS spectrometer.[7]

The reaction of ·OH with 2,5-dihydrofuran in the presence of oxygen was also studied in reactors A and C with similar methods.

Photolysis of the mixture, $H_2O_2/^{18}O_2/N_2$/diolefin, was carried out several times in reactor A and isotopic product analysis was made by means of GC-MS with the same procedure as for mass spectroscopic identification.

1,3-Butadienen was from Takachiho Kagaku. Acetaldehyde, acrylaldehyde, crotonaldehyde, furan, 2-methylfuran, *cis*-1,3-pentadiene, and 2,5-dihydrofuran were purchased from Tokyo Kasei. They were degassed before use by trap to trap distillation. Heavy oxygen ($^{18}O_2$, 98.6%) was obtained from Merck Frosst Canada and the purity was confirmed by means of mass spectrometer and the detected impurity was only $^{16}O^{18}O$. Research grade N_2 and O_2 were from Nippon Sanso.

Results

Typical gas chromatograms for the products in the photooxidation of either 1,3-butadiene or *cis*-1,3-pentadiene with H_2O_2 are shown in Figs. 1 and 2, respectively, together with identified compounds. It is noteworthy that Porapak Q or R could not separate acrylaldehyde and furan produced in the reaction of 1,3-butadiene. Each peak had GLC elution times, mass spectra, and infrared spectra identical with those of the respective commercial samples. The identified products under our experimental conditions were furan (C_4H_4O), and acrylaldehyde (C_2H_3CHO) in the reaction of 1,3-butadiene (C_4H_6) and 2-methylfuran (C_5H_6O), acetaldehyde (CH_3CHO), acrylaldehyde, and crotonaldehyde (C_3H_5CHO) in the reaction of *cis*-1,3-pentadiene (C_5H_8).

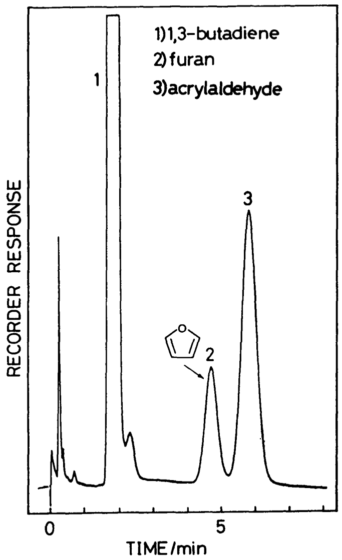


Fig. 1. Typical gas chromatogram of the products in the photolysis of the mixture, H_2O_2[1.0 Torr]/1,3-butadiene[0.4 Torr]/O_2[760 Torr], at 254 nm.

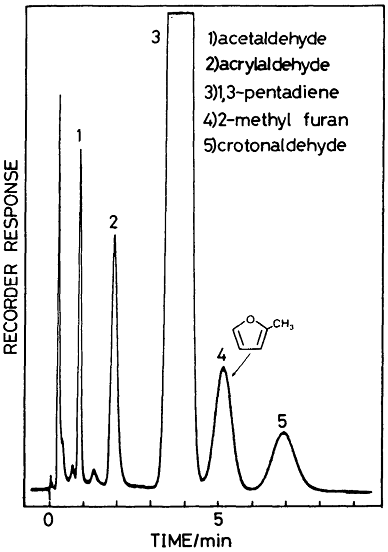


Fig. 2. Typical gas chromatogram of the products in the photolysis of the mixture, H_2O_2[1.0 Torr]/*cis*-1,3-butadiene[0.3 Torr]/O_2[760 Torr], at 254 nm.

For the reaction systems in which H_2O_2 was used as radical source, the reaction cell was kept in the dark after a few minutes irradiation and the concentration of products were measured intermittently. It was observed that furan and 2-methylfuran increased gradually until about 50 min after a few minutes irradiation, while aldehydes remained almost constant (Fig. 3). The yield of furans was determined after the cease of the formation in the dark and the yield of other compounds was determined from the first injection to GC about 30 s after turning off the lamps. For the runs at low pressures, nitrogen was filled upto 760 Torr just after photolysis and gas chromatographic analysis was made. Since it was noticed that furans yield became somewhat larger as the conditioning of the wall surface of reaction cell was improved by repeating the experiments, these series of runs were made after conditioning the surface of the reactor A well. The product yield obtained with various initial conditions is presented in Table 1 for the 1,3-butadiene system and in Table 2 for the *cis*-1,3-pentadiene system. The increase of furan after the photolysis observed for Runs 1 to 6 in Table 1 is shown in Fig. 3. Product yield at 760 Torr total pressure was almost independent of the variation of the initial concentrations of reactants, or of the addition of one of products. But pressure effect was observed: at low total pressure around 2.5 Torr, the yield of furans increased and that of aldehydes decreased (Tables 1 and 2). The difference observed in the pressure effect indicates that some fraction of furan and 2-methylfuran, at least, was not formed *via* initial ·OH addition to the double bonds.

Figure 4 shows the product yield after 1.5 min irradiation of the mixture CH_3ONO [1.0 Torr]/1,3-butadiene [0.27 Torr]/O_2 [760 Torr] in comparison

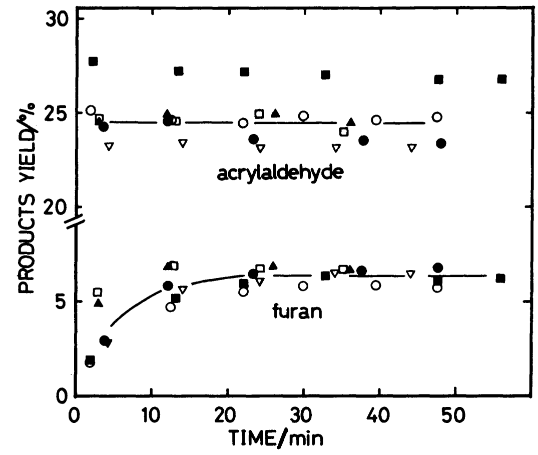


Fig. 3. Dark increase of furan after 1.5—3.0 min irradiation of the mixture H_2O_2/1,3-butadiene/O_2 for Runs 1 to 6 in Table 1.

TABLE 1. PRODUCTS YIELD IN THE PHOTOLYSIS OF H_2O_2/1,3-BUTADIENE/O_2 WITH DIFFERENT INITIAL CONDITIONS

Run	Irrad. time	Reactants (Torr)				P_t	Products yield/%	
	min	C_4H_6	H_2O_2	O_2	Added gas		C_4H_4O	C_2H_3CHO
1	1.5	.407	1.0	1.1	—	760	5.55	25.2
2	1.5	.409	1.0	1.1	—	760	6.18	27.8
3	1.5	.361	1.0	759	—	760	6.59	23.4
4	1.5	.368	1.0	759	—	760	6.68	24.4
5	3.0	1.38	1.0	758	—	760	6.50	23.2
6	3.0	1.39	1.0	758	—	760	6.96	23.5
7	1.5	.404	1.0	1.1	Acrl[a], .341	760	7.19	—
8	1.5	.401	1.0	1.1	Acrl[a], .341	760	7.40	—
9	3.0	.381	.48	1.1	—	760	7.53	29.6
10	3.5	.399	.47	1.1	—	760	7.62	27.9
11	1.5	.306	1.0	1.1	—	2.4	10.5	20.6
12	1.5	.314	1.0	1.1	—	2.4	11.4	21.1

a) Acrylaldehyde.

TABLE 2. PRODUCTS YIELD IN THE PHOTOLYSIS OF H_2O_2/*cis*-1,3-PENTADIENE/O_2 WITH DIFFERENT INITIAL CONDITIONS

Run	Irrad. time	Reactants (Torr)				P_t	Products yield/%			
	min	C_5H_8	H_2O_2	O_2	Added gas		C_5H_6O	CH_3CHO	C_2H_3CHO	C_3H_5CHO
1	2.0	.322	1.0	759	—	760	7.12	13.2	12.2	8.33
2	2.0	.315	1.0	759	—	760	8.45	14.8	13.3	10.1
3	2.0	3.59	1.0	755	—	760	8.11	12.2	13.2	10.3
4	2.0	1.89	1.0	757	—	760	6.84	11.9	12.3	9.87
5	2.0	.340	1.0	9.0	—	760	8.85	15.9	14.6	11.4
6	2.0	.342	1.0	9.0	—	760	9.39	16.4	14.5	11.8
7	3.5	.306	.48	9.0	—	760	9.25	16.7	14.2	9.80
8	3.0	.299	.44	9.0	—	760	9.13	17.4	14.6	11.7
9	2.0	.330	1.0	9.0	Acet,[a] .371	760	13.1	—	14.2	12.4
10	3.0	.330	1.0	9.0	Acet, .428	760	11.4	—	13.0	10.8
11	3.0	.332	1.0	9.0	Acrl, .540	760	9.88	19.2	—	9.12
12	2.5	.336	1.0	9.0	Acrl, .337	760	10.4	17.2	—	9.81
13	3.0	.330	1.0	8.5	Crot, .455	760	11.1	—	16.9	—
14	3.0	.330	1.0	8.5	Crot, .418	760	9.92	—	15.9	—
15	2.0	.367	1.0	1.2	—	2.6	10.3	8.44	8.79	6.54
16	3.0	.367	1.0	1.2	—	2.6	9.71	9.41	9.63	7.33

a) Acet=acetaldehyde, Acrl=acrylaldehyde, Crot=crotonaldehyde.

with the results for the mixture H_2O_2 [1.0 Torr]/1,3-butadiene [0.3 Torr]/O_2 [760 Torr]. It was noticed that the yield of acrylaldehyde was larger and the increase of furan in the dark was faster in the CH_3ONO system than in the H_2O_2 system and that 1,3-butadiene was consumed by NO_2 in the dark. The addition of a proper amount of NO to the CH_3ONO system made the increase of furan in the dark stop and the consumption of 1,3-butadiene in the dark more significant. These facts indicate that some peroxy radicals exist as intermediate compounds to form furan.

In order to examine the wall effect on the reaction, product yield for both ·OH sources in different five reactors were measured and summarized in Tables 3 and 4, for the 1,3-butadiene and for the *cis*-1,3-pentadiene systems, respectively. Irradiation was usually 1 to 2 min for the runs in reactors A to D, and it was 10 to 15 min in reactor E. In the latter case, the yield was corrected by considering the consumption of the diolefins with the dark reactions of NO_2 in CH_3ONO system. The yield of CH_3CHO in CH_3ONO/*cis*-1,3-pentadiene system was lower limit, since the peak of CH_3CHO was on the shoulder of large peak of CH_3ONO in gas chromatogram and the peak height of CH_3CHO was measured from the higher valley rather than ambiguous lower valley. Throughout this series, wall surface was kept rather clean without repeating extra runs. The results showed that the yield of furan and 2-methylfuran was almost independent of the surface material of the reactors or the surface to volume ratio of reactors, or ·OH radical sources, whereas aldehydes yield in the CH_3ONO system was larger than that in the H_2O_2 system. Larger yield of acrylaldehyde in the photolysis of CH_3ONO/1,3-butadiene may be attributed to the faster reaction of NO with peroxy radicals to produce alkoxy radicals which are the precursors of acrylaldehyde than the reactions between some peroxy radicals to lead unspecified products. Since no definite dependence of the yield of furans on S/V of reactors was measured, the discrepancy of the yield in the clean reactor (Tables 3 and 4) and well conditioned reactor (Tables 1 and 2) may be attributed to other reasons: for example, conditioning of the surface would suppress the wall decay of the intermediate working as reservoir of the precursor radicals of furans.

Results for several isotopic labeling experiments with heavy oxygen are summarized in Tables 5 and 6 for the photolysis of H_2O_2/1,3-butadiene/$^{18}O_2$/N_2 and H_2O_2/*cis*-1,3-pentadiene/$^{18}O_2$/N_2 respectively. Before and after the photolysis, a small fraction of the reaction mixture in the reactor was analyzed by mass spectrometer. Oxygen-16 molecule was not detected in the mixture before the irradiation, and very small amount of $^{16}O_2$ (less than 5%) was detected after the photolysis in some runs. Addition of NO changed the ratio of labeled aldehyde, but the yield for labeled furans was not affected.

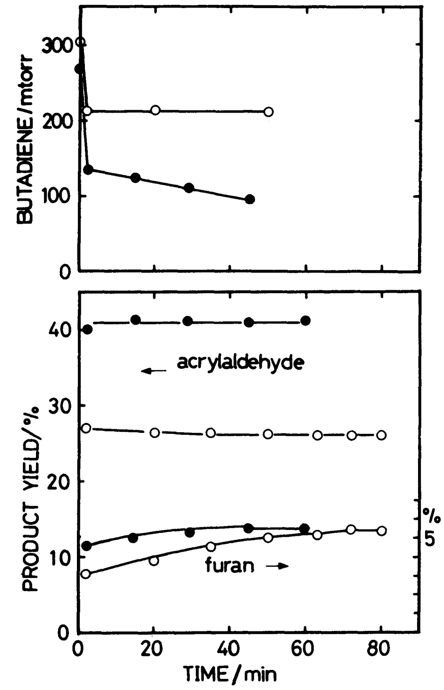


Fig. 4. Difference in the dark reactions after 1.5 min irradiation at 360 nm of the mixture of CH_3ONO[1.0 Torr]/1,3-butadiene[0.27 Torr]/O_2 [760 Torr], (closed circle) and after 1.5 min irradiation at 254 nm of the mixture of H_2O_2[1.0 Torr]/1,3-butadiene[0.30 Torr]/O_2[760 Torr], (open circle).

Discussion

Detection of both ^{18}O-aldehydes and ^{16}O-aldehydes suggests that ·OH addition to nonterminal double-bond carbon atom also occurs as well as to the terminal carbon atom against the assumption of the occurrence of only terminal addition by Maldotti *et al.*[3] In view of the low yield of the detected products, undetected products by our method, such as hydroxy ketones, hydroxy aldehydes and other compounds, might be produced. As an example, possible ·OH addition steps to 1,3-butadiene are shown in Reactions 4 and 5 (O* indicates ^{18}O).

$$\mathrm{C{=}C{-}C{=}C+OH \rightarrow C(OH){-}C{-}C{=}C \xrightarrow{O_2^*} CH_2O+C_2H_3CHO^*} \quad (4)$$
$$\rightarrow \text{unspecified products}$$

$$\mathrm{C{-}C(OH){-}C{=}C \xrightarrow{O_2^*} CH_2O^*+C_2H_3CHO} \quad (5)$$
$$\rightarrow \text{unspecified products}$$

Table 3. Products yield in the photolysis of OH with 1,3-butadiene in different reactors

Reactor[a]	Reactants[b] (Torr)			Products yield/%	
	C_4H_6	CH_3ONO	H_2O_2	C_4H_4O	C_2H_3CHO
A	.286	.25	—	6.51	41.8
A	.283	.78	—	5.61	38.2
B	.267	.83	—	5.80	42.5
B	.272	.86	—	5.67	39.5
C	.300	.40	—	5.04	37.0
C	.341	.65	—	5.12	32.9
D	.361	.62	—	5.28	33.2
E	.412	.24	—	4.00	32.4
E	.476	.08	—	5.70	54.3
A	.303	—	1.0	5.47	26.1
A	.285	—	1.0	4.91	25.6
B	.302	—	0.9	4.92	23.4
B	.277	—	0.7	5.40	25.2

a) See the Experimental section in the text.
b) Oxygen was added up to 760 Torr.

Table 4. Products yield of the reaction of OH with *cis*-1,3-pentadiene in different reactors

Reactor[a]	Reactants[b] (Torr)			Products yield/%			
	C_5H_8	CH_3ONO	H_2O_2	C_5H_6O	CH_3CHO	C_2H_3CHO	C_3H_5CHO
A	.204	.90	—	6.57	>18.2	17.4	9.89
A	.224	.57	—	7.32	>16.2	17.4	8.27
B	.206	.97	—	7.70	>12.0	19.7	13.5
B	.188	1.6	—	7.57	>16.3	18.5	11.3
C	.226	.55	—	5.62	>14.4	16.2	9.73
C	.261	.65	—	5.89	>15.1	17.2	9.04
D	.271	.67	—	6.01	>11.7	16.0	6.09
E	.340	.07	—	5.04	>18.0	19.2	9.00
E	.501	.27	—	5.50	>20.0	21.0	9.60
A	.291	—	1.0	4.72	14.0	13.0	8.45
A	.309	—	1.0	6.32	15.7	12.9	8.30
B	.321	—	0.8	5.96	14.7	13.2	8.61
B	.347	—	0.8	6.38	15.7	14.2	10.5

a) See the Experimental section in the text. b) Oxygen was added up to 760 Torr.

TABLE 5. ISOTOPIC PRODUCTS ANALYSIS OF THE PHOTOLYSIS OF 1,3-BUTADIENE/H_2O_2/$^{18}O_2$/N_2 AT 760 Torr

Run	Irrad. time	Reactants (Torr)				^{18}O-Products ratio/%	
	min	C_4H_6	H_2O_2	$^{18}O_2$	Added gas	C_4H_4O	C_2H_3CHO
1	27	.217	1.4	9.6	—	32	78
2	25	.180	0.9	>9.0	—	38	83
3	15	1.06	1.0	>8.2	—	37	90
4	20	1.08	1.0	8.0	NO, .262	44	49

a) [^{18}O-product]/([^{18}O-product]+[^{16}O-product])$\times$100.

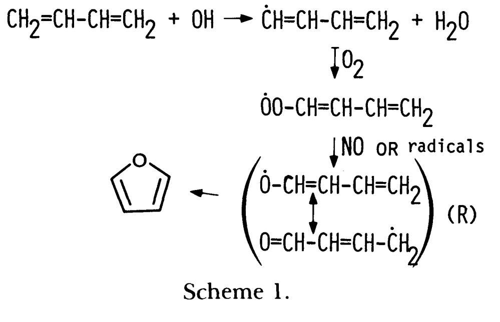
TABLE 6. ISOTOPIC PRODUCTS ANALYSIS OF THE PHOTOLYIS *cis*-1,3-PENTADIENE/H_2O_2/$^{18}O_2$/N_2 AT 760 Torr

Run	Irrad. time	Reactants (Torr)				^{18}O-Products ratio/%$^{a)}$			
	min	C_5H_8	H_2O_2	$^{18}O_2$	Added gas	C_5H_6O	CH_3CHO	C_2H_3CHO	C_3H_5CHO
1	22	2.03	1.3	9.9	—	42	25	78	80
2	25	0.49	1.0	>8.7	—	48	18	83	80
3	15	0.53	1.0	>8.3	NO, .083	40	19	67	42
4	21	0.36	1.1	8.6	NO, .262	38	9	36	56

a) [^{18}O-product]/([^{18}O-product]+[^{16}O-product])$\times$100.

Formation of ^{16}O-furan and ^{18}O-furan in isotopic labeling experiments suggests that two pathways for the formation of furans at least exist. Furan (C_4H_4O) has two less hydrogen atoms than the parent molecule, 1,3-butadiene(C_4H_6), and also *cis*-1,3-pentadiene (C_5H_8) must lose two hydrogen to form 2-methylfuran (C_5H_6O). The fact that the pressure effect on the formation of furans was observed adversely to the pressure effect on the formation of aldehydes indicates that the ways of initial attack to diolefins by ·OH were different for the two processes. Furthermore, the fact that the addition of NO changed the ratios of ^{18}O labeled aldehydes significantly but did not affect those for furans suggests that the precursors for ^{18}O-furan might be consumed by single pathway without competitive reactions to lead other products. Therefore, it is reasonable to assume that one of the terminal vinyl-hydrogen was abstracted by ·OH radicals in the first step and, then, $^{18}O_2$ added to the unpaired elctron on the radicals and that through some radical-radical reactions, an alkoxy radical, ·R in Scheme 1, was formed. The radical was stabilized by resonance as shown in Scheme 1, and a new bond would be formed between the two radical centers to make furan rings.

Some semi-quantitative discussions on the abstraction pathway in diolefins are tried by comparing with the abstraction pathway in ethylene and benzene. Average yield of furan determined from the runs at 760 Torr without added gas (Runs 1—6 in Table 1) was 6.7% and that of 2-methylfuran was 8.4% from Runs 1—8 in Table 2. And average mixing ratio of labeled furan was 38% from Table 3 and that of labeled 2-methylfuran was 42% from Table 4. Thus, the abstraction of vinyl-hydrogen in 1,3-butadiene occurred 2.5% ($=6.7\times 0.38$) of the time and the abstraction in *cis*-1,3-pentadiene occurred 3.5% of the time. This fairy larger contribution of the abstraction pathway to the overall rate constants was surprising. Overall rate constants for the reaction of ·OH with 1,3-butadiene[8] and *cis*-1,3-pentadiene[4] were 68.5×10^{-12}, 103×10^{-12} cm^3 mol^{-} S^{-1}, respectively. The assigned rate constants for the abstraction of the vinyl-hydrogen were 1.7×10^{-12}($=68.5\times10^{-12}\times0.025$) and 3.6×10^{-12} cm^3 mol^{-1} s^{-1}, respectively. The contribution of the abstraction of one vinyl-hydrogen in 1,3-butadiene was 4.3×10^{-13} ($=1.7\times10^{-12}/4$) cm^3 mol^{-1} s^{-1}, which is larger than the contribution of the abstraction of a primary C–H bond in alkane by a factor of 6.6,[1] whose bond dissociation energy (BDE) is 98 kcal mol^{-1} (1 cal=4.18 J) and smaller than BDE of C_4H_5–H. Concerning the abstraction of vinyl-hydrogen in ethylene by ·OH, which is exothermic by 11 kcal mol^{-1},[9] two different views have been proposed: BDE(H–C_2H_3)=108, BDE(H–OH) 119 kcal mol^{-1}. Meagher and Heicklen[10] reported that the hydrogen abstraction reaction contributed 26% of the total reaction pathway under their experimental conditions from the analysis of the formic acid yield. However, Atkinson *et al.*[1] concluded that the contribution of the abstraction was very minor in consideration of the comprehensive product study of the reaction of ·OH with propylene by Cevetanovic[11] and the rate constant study of Howard:[12] Howard has shown from a determination of the absolute rate constant for the reaction of ·OH with ethylene over the total pressure range of 0.7—7 Torr of helium, that abstraction of vinyl-hydrogen at room temperature is implied to be negligible, because the rate constant for



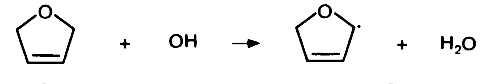
Scheme 1.

ethylene extrapolates to essentially zero at zero pressure. As for hydrogen abstraction by ·OH radicals in benzene, Perry *et al.*[13] reported that the occurrence of the reaction was 1—8% of the time from the study on the temperature dependence of the rate constant. Carbon-hydrogen bond energy in benzene is 110.5 kcal mol^{-1}.[9] If we assume the bond energy of C–H in 1,3-butadiene similar to that in ethylene and benzene, the observed value in 1,3-butadiene appeared to be larger than that expected from the previous works. However, the detection of labeled furans evidently suggests the occurrence of the abstraction of vinyl-hydrogen by ·OH radicals in 1,3-butadiene and *cis*-1,3-pentadiene. But it is obviously necessary to detect directly the abstracted radicals (C_4H_5· and C_5H_7·) by means of more sophisticated techniques, such as flow system coupled to photoionization mass spectrometer.

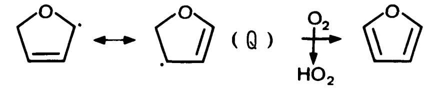
The mechanism for the formation of ^{16}O–furanes remains unclear in this work. But it is reasonable to assume that ^{16}O came from ·OH radicals and ·OH–diolefin adducts were precursors for furans, since H_2O_2 did not react with the studied conjugated dienes in the dark.

The increase of furans in the dark after irradiation may be attributed to the decomposition of some complexes formed by reversible recombination reactions of peroxy radicals. Benson described[14] that usual alkyl radicals would irreversibly combine with oxygen molecule to become peroxy radicals followed by some reactions to form oxygen containing compound *via* some complexes of peroxy radicals. He also suggested[14] that unsaturated resonance-stabilized radicals, such as allyl and benzyl radicals, would have much smaller equilibrium constant in the combination reaction with O_2, and that back reaction might become important. In the reaction systems studied here, the unsaturated resonance-stabilized radicals, ·R in Scheme 1, and/or other unknown precursors of ^{16}O-furan would combine to form some metastable compound as reserviors for radicals, and, after turning off the lamps, the metastable complex would decompose to produce the initial radicals or the other precursors.

In order to support this assumption, similar size resonance-stabilized radicals were produced and it was examined whether the increase of the products in the dark was observed or not: the reaction of ·OH with 2,5-dihydrofuran (DHF) in the presence of oxygen was studied. DHF has four labil allylic hydrogens for ·OH attack to form radical ·Q in Reaction 6. The radical ·Q is expected to be stabilized by resonance and to lose another hydrogen by O_2 to ultimately form furan (Reaction 7).



(6)



(7)

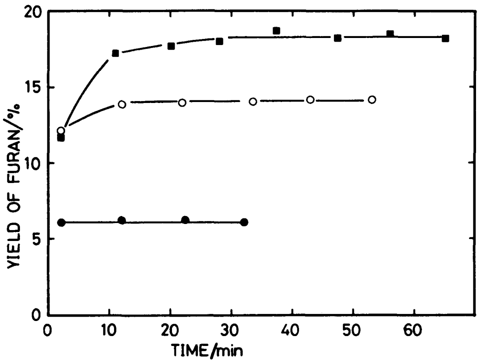


Fig. 5. Dark increase of furan after 1.5 min irradiation of 2,5-dihydrofuran (DHF): initial concentrations (torr): DHF, 0.19; H_2O_2, 1.0; O_2, 760 (closed squares): DHF, 0.32; CH_3ONO, 0.82; O_2, 760 (open circles): DHF, 0.35; CH_3ONO, 0.76; NO, 0.05; O_2, 160; N_2, 600 (closed circle).

By use of a similar procedure used for 1,3-butadiene, the mixture, H_2O_2[1.0 in Torr]/DHF[0.19]/O_2[760], CH_3ONO[0.82]/DHF[0.32]/O_2[760], and NO[0.05]/CH_3ONO[0.76]/DHF[0.35]/O_2[160]/N_2[600], were photolyzed. The detected product under this gas chromatographic condition was only furan. The plots of the yield of furan *vs.* time are shown in Fig. 5. Furan showed increase in the dark after 1.5 min irradiation in the absence of NO, similar to the reactions of the diolefins. However, the addition of NO to the mixture, CH_3ONO/DHF, before the irradiation suppressed the increase of furan in the dark. Thus, the increase of furan in the dark may be explained by the similar assumption that some fraction of ·Q combined with O_2 to form ·QO_2 and that the ·QO_2 radicals were stored as some metastable complexes with fairy large lifetime and, then, the complex decomposed to ·QO_2 and supplied ·Q in the system to form furan even in the dark *via* Reaction 7. Addition of NO to the mixture made ·QO_2 quenched to ·QO to lead other unspecified products. Therefore, it is reasonable to assume that some unsaturated resonance-stabilized radicals consisting of four carbon and an oxygen atom form some metastable compound in the presence of oxygen whose lifetime is in the order of minutes in our reactors. Spectroscopic technique will be able to detect the complexes.

Ring formation from the reaction of 1,3-butadiene with sulfur atoms,[15] and nitrogen atoms[16] were reported. The formation of thiophene was proposed to proceed mainly *via* sulfur atom addition in the 1,2-positions and lose two hydrogens unimoleculary.[15] The formation mechanism of pyrrole was not presented in the paper.[16] Furan was not detected in the reaction of oxygen atoms (^{3}P) with 1,3-butadiene.[17] There still remain uncertainties in the mechanism for the formation of furan type compound from the reactions of radicals with 1,3-butadiene.

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