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Reactions of Methyl Radicals with Oxetan, 2-Methyloxetan and 2,4-Dimethyloxetan

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The reactions of methyl radicals with oxetan, 2-methyloxetan and 2,4-dimethyloxetan have been studied. The overall rates of hydrogen atom abstraction from these three compounds have been obtained for the temperature range 100-200°C, by assuming the value of Quinn and co-workers for the rate of recombination of methyl radicals.

The following rate expressions were found:

$$\log_{10}(k/\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1})_{(\text{ox})} = 11.29(\pm 0.19) - 35.22(\pm 0.64)\,\text{kJ mol}^{-1}/2.303RT$$

$$\log_{10}(k/\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1})_{(2\text{ox})} = 11.42(\pm 0.18) - 34.04(\pm 0.62)\,\text{kJ mol}^{-1}/2.303RT$$

$$\log_{10}(k/\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1})_{(2,4\text{ox})} = 11.51(\pm 0.18) - 33.52(\pm 0.69)\,\text{kJ mol}^{-1}/2.303RT.$$

The results are compared with those for other hydrogen abstraction reactions by methyl radicals and the implications for the gas phase thermolyses of substituted oxetans are discussed.

Recent work[1, 2] on the thermolysis of substituted oxetans has revealed the presence of small amounts of minor products attributable to radical attack on the parent oxetan molecule. Apart from the work of Margerum *et al.*,[3] no direct studies have been reported of the reactions between methyl radicals and oxetans and very little information exists generally[4] on the abstraction reactions of methyl radicals with cyclic molecules. We have therefore undertaken a study of the reactions of methyl radicals with a variety of substituted oxetan molecules, principally in order to establish the Arrhenius parameters for attack at various sites. In the present paper we present the results for oxetan and two related methyl-substituted oxetans which enable information concerning three different types of hydrogen atoms to be obtained.

EXPERIMENTAL

APPARATUS AND PROCEDURE

The experiments were carried out in the gas phase by photolysing reaction mixtures in a Pyrex cell (vol. 180 cm³) with a plane glass window. The cell was enclosed in a furnace with a quartz window and the temperature was controlled to ±0.3°C by a Sunvic RT3 resistance thermometer. A chromel–alumel thermocouple, referenced in iced water, was used to measure the temperature.

Methyl radicals were generated by the photolysis of acetone using a medium pressure mercury lamp (Hanovia). A parallel light beam was produced by using a 5 cm diameter quartz lens of focal length 17 cm; wavelengths were restricted to 300 nm and above by having a Pyrex-shielded lamp. The reaction cell was connected to a conventional static vacuum system with a sampling valve permitting on-line g.l.c. analysis using a Pye GCD chromatograph. Known mixtures of acetone and oxetan were admitted to the reaction cell and, after allowing the lamp to reach maximum intensity, the light beam was allowed to enter the reaction cell. Photolysis times were usually 1800 s, but other times were used to check that the rates of formation of CH_4 and C_2H_6 were unaffected by time. Pressures of the reactants were measured by an SEL 1150 D pressure transducer. At the end of the time of photolysis the reaction products were analysed quantitatively by g.l.c. for CH_4, C_2H_6, C_2H_4 and C_3H_6. The products were determined using a 5 ft glass column of 3 % di-2-ethylhexylsebacate on 60-80 mesh silica-gel operated at 60°C with a nitrogen flow-rate of 40 cm^3 min^{-1}.

Carbon monoxide was analysed using a Varian Aerograph 1532-2B helium-ionisation chromatograph with a 3 m molecular sieve type 5A (30-60) mesh column, operated at 50°C.

MATERIALS

Acetone (A.R.) was supplied by Koch-Light and, after thorough degassing and on-line distillation, was found to be > 99.5 % pure.

Oxetan was supplied by Aldrich Chemicals and, after thorough degassing and on-line distillation, was found to be > 99.5 % pure.

The 2-methyloxetan was a gift from Dr. M. Bartok (University of Szeged, Hungary) and was > 99.5 % pure.

The 2,4-dimethyloxetan was prepared in these laboratories by Mrs. B. Worthington. Pentan-2,4-dione was reduced to pentan-2,4-diol and converted into its bromo ester by adding acetylbromide. This was ring-closed to the product by stirring with tributyltin oxide[5] at 220°C for 2 h.

Methane and carbon monoxide for calibrations were supplied by Air Products. Ethane, ethene and propene for calibrations were supplied by Cambrian Chemicals. All these gases were shown to be > 99 % pure.

RESULTS

PHOTOLYSIS OF ACETONE

The photolysis of acetone was studied at temperatures from 100 to 192°C and at pressures from 5 to 60 Torr * as a check on the apparatus and technique.

The accepted mechanism[6] for this photolysis above 100°C is

$$CH_3COCH_3 \xrightarrow{h\nu} 2CH_3+CO$$

$$CH_3+CH_3COCH_3 \xrightarrow{k_1} CH_4+CH_2COCH_3 \qquad (1)$$

$$CH_3+CH_2COCH_3 \xrightarrow{k_2} C_2H_5\,COCH_3 \qquad (2)$$

$$2CH_3 \xrightarrow{k_3} C_2H_6. \qquad (3)$$

This leads to the expression

$$\frac{R_{CH_4}}{R^{\frac{1}{2}}_{C_2H_6} \times P_{acetone}} = k_1/k_3^{\frac{1}{2}}$$

where R_{CH_4} and $R_{C_2H_6}$ are the rates of formation of methane and ethane, respectively. Our results, together with the rate constant for methyl recombination measured by Quinn and co-workers,[7] *i.e.*,

$$k_3 = 2.41(\pm 0.54) \times 10^{13}\ cm^3\ mol^{-1}\ s^{-1},$$

leads to the rate expression

$$\log_{10}(k_1/cm^3\ mol^{-1}\ s^{-1}) = 11.52(\pm 0.19) - 40.32(\pm 0.49)\ kJ\ mol^{-1}/2.303\boldsymbol{RT}$$

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* 1 Torr = 133.33 Pa.

(the error limits being the 95 % confidence limits), which is in good agreement with the results of Ferguson and Pearson [8]

$$\log_{10}(A/\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 11.50(\pm 0.1),\ E = 40.33(\pm 0.79)\ \text{kJ mol}^{-1}$$

and of Gray and Herod [9]

$$\log_{10}(A/\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 11.46(\pm 0.07),\ E = 40.33(\pm 0.33)\ \text{kJ mol}^{-1}.$$

REACTIONS BETWEEN METHYL RADICALS AND OXETANS

When acetone is photolysed in the presence of an oxetan the additional hydrogen abstraction reaction (4) occurs.

$$\text{CH}_3 + \text{oxetan} \xrightarrow{k_4} \text{oxetanyl} + \text{CH}_4. \qquad (4)$$

Inclusion of this reaction in the above scheme leads to the expression

$$\frac{R_{\text{CH}_4}}{R^{\frac{1}{2}}_{\text{C}_2\text{H}_6} \times P_{\text{acetone}}} = \frac{k_1}{k_3^{\frac{1}{2}}} + \frac{k_4}{k_3^{\frac{1}{2}}} \times \frac{P_{\text{oxetan}}}{P_{\text{acetone}}}.$$

Plots of the left-hand side of this expression against $P_{\text{oxetan}}/P_{\text{acetone}}$ are shown, for the three oxetans studied, in fig. 1. This expression predicts linear plots provided that P_{oxetan} and P_{acetone} are not depleted by formation of products during the experiment. This is shown by the data in tables 1 and 2.

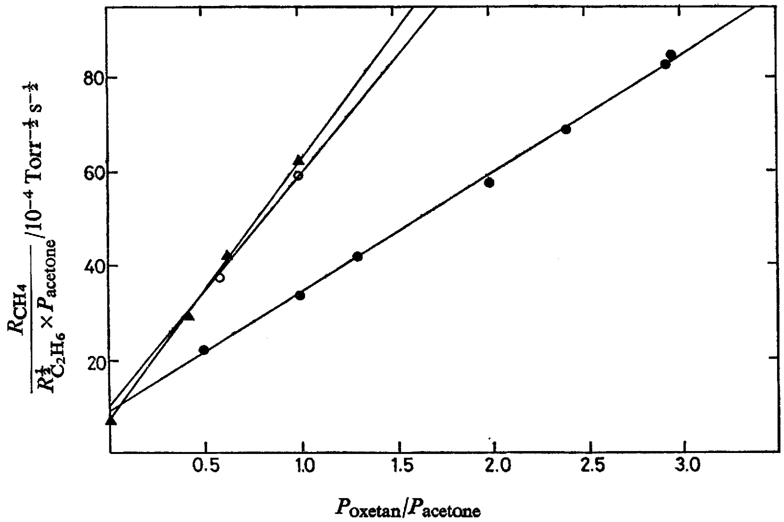


FIG. 1.—Plots for calculation of $k_4/k_3^{\frac{1}{2}}$. ●, oxetan at 134.6°C; ○, 2-methyloxetan at 137°C; ▲, 2,4-dimethyloxetan at 126°C.

In all three cases the oxetan under study was illuminated alone for 1 h at 150°C and no products were detected. The three oxetans were also put separately into the furnace and left for 1 h without illumination to check that there was no thermal decomposition; no breakdown products were detected.

OXETAN

An acetone pressure of 30 Torr was used at 100°C and adjusted accordingly to keep the initial concentration constant as the temperature was raised. Most experiments were carried out at an oxetan to acetone ratio of 1.0, although several photolyses were carried out at a ratio of less than 1.0 to show that $k_4/k_3^{\frac{1}{2}}$ was independent of this ratio (see fig. 1). From a series of 23 photolyses in the temperature range 100.2-191.8°C, the rate constant for the overall abstraction of hydrogen from oxetan is given by

$$\log_{10}(k_4/\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1})_{(\text{ox})} = 11.29(\pm 0.19) - 35.22(\pm 0.64)\ \text{kJ mol}^{-1}/2.303RT,$$

the error limits being the 95 % confidence limits. The values of $k_4/k_3^{\frac{1}{2}}$ used for the Arrhenius plot (fig. 2) are shown in table 1.

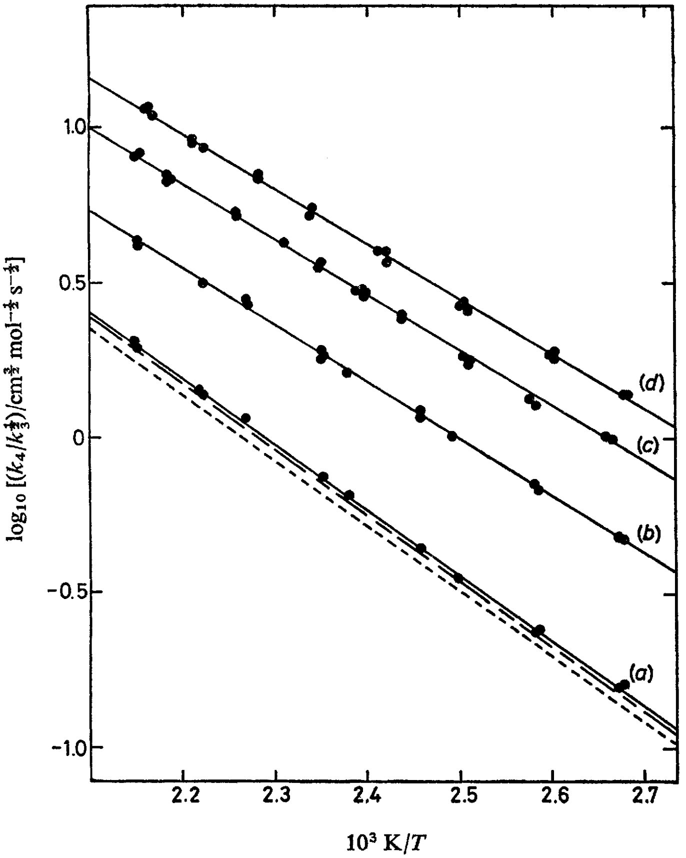
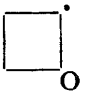


FIG. 2.—Arrhenius plots. (*a*) acetone, (——) this work, (— - —) ref. (8), (- - -) ref. (9); (*b*) oxetan; (*c*) 2-methyloxetan; (*d*) 2,4-dimethyloxetan.

As well as methane and ethane, ethene, carbon monoxide and hydrogen were found in the reaction products. Ethene and carbon monoxide were determined quantitatively, but hydrogen was only detected at temperatures above 160°C and no accurate quantitative work could be done. The carbon monoxide formed was determined by subtracting the pressure of CO measured by the photolysis of acetone. Due to the small pressures of CO involved and the method of measurement, errors are likely to be quite large. At all temperatures, the ethene pressure was equal, within experimental error, to the carbon monoxide pressure (after correction for the CO formed from acetone), as shown for three temperatures in table 2, which is in accordance with the break down of the 2-oxetanyl radical, as shown.



$\rightarrow C_2H_4 + H\dot{C}O$

$$H\dot{C}O \rightarrow CO + H.$$

The analogous breakdown of the 3-oxetanyl radical to give formaldehyde and a vinyl radical was considered to be slow under the conditions used by Margerum *et al.*[3] due to the absence of propene and butadiene and the relatively small amounts of formaldehyde formed. No propene was found in our products, but formaldehyde and butadiene were not specifically tested for.

TABLE 1.—ANALYTICAL RESULTS AND RATE CONSTANT RATIOS FOR THE METHYL RADICAL–OXETAN REACTION

T/°C	p_{acetone} /Torr	p_{oxetan} /Torr	p_{CH_4} /10^{-2} Torr	$p_{C_2H_6}$ /10^{-2} Torr	$k_4/k_3^{\frac{1}{2}}$ /$\text{cm}^{\frac{3}{2}}$ $\text{mol}^{-\frac{1}{2}}$ $\text{s}^{-\frac{1}{2}}$
100.2	29.9	30.6	2.89	2.89	0.477
100.8	30.3	30.3	3.03	3.14	0.482
113.3	31.7	31.7	4.07	2.61	0.681
113.4	31.7	31.4	4.26	2.78	0.689
114.1	31.3	31.3	4.24	2.73	0.711
114.2	31.6	31.6	4.29	2.76	0.706
128.0	31.9	31.9	6.35	2.83	1.01
133.6	32.4	32.2	6.37	2.02	1.20
133.7	32.7	19.4	5.09	2.68	1.16
133.7	32.7	32.6	6.49	2.00	1.23
147.0	32.6	32.6	8.62	1.97	1.61
147.0	32.6	32.6	8.87	2.04	1.65
147.1	32.6	23.1	7.93	2.68	1.60
151.8	34.2	34.5	9.46	1.66	1.84
152.3	33.9	17.6	7.83	2.79	1.82
152.3	34.2	34.5	10.01	1.81	1.91
166.7	35.8	18.4	9.96	1.86	2.72
167.2	35.7	35.5	11.7	1.10	2.73
167.5	35.2	35.7	11.7	1.07	2.78
176.7	36.6	38.4	12.3	0.789	3.21
177.0	36.6	36.8	12.6	0.873	3.19
191.8	37.3	21.2	10.9	0.712	4.19
191.8	37.5	14.7	9.81	0.806	4.31

TABLE 2.—EQUIVALENCE OF ETHENE AND CARBON MONOXIDE

T/°C	p_{CO} total /10^{-2} Torr	p_{CO} from oxetan /10^{-2} Torr	$p_{C_2H_4}$/10^{-2} Torr
133.7	5.35	1.04	0.938
147.0	7.62	1.86	1.83
152.3	8.28	2.44	2.57

2-METHYLOXETAN AND 2,4-DIMETHYLOXETAN

From a series of 30 photolyses in the temperature range 102.1-192.9°C the rate constant for overall hydrogen abstraction by methyl radicals from 2-methyloxetan is given by

$$\log_{10}(k_4/\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1})_{(2\text{ox})} = 11.42(\pm 0.18) - 34.04(\pm 0.62)\ \text{kJ mol}^{-1}/2.303RT,$$

the error limits being 95 % confidence limits. Only qualitative analyses were carried out for CO and H_2, but ethene and propene were analysed quantitatively. The ethene path was favoured, but the ratio of ethene : propene was found to depend on temperature, being 2.2±0.1 at 115°C and 1.5±0.1 at 192°C.

For 2,4-dimethyloxetan, 29 photolyses were carried out in the temperature range 99.9-189.2°C and the rate constant for overall hydrogen abstraction by methyl radicals is given by

$$\log_{10}(k_4/\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1})_{(2,4\text{ox})} = 11.51(\pm 0.18) - 33.52(\pm 0.69)\ \text{kJ mol}^{-1}/2.303RT,$$

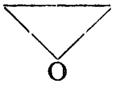
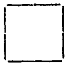
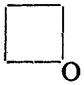
the error limits being the 95 % confidence limits.

DISCUSSION

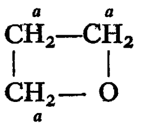
The Arrhenius parameters obtained for the abstraction reaction (1) are in very close agreement with those reported by other workers [8, 9] and this gives us some confidence in our apparatus and procedure.

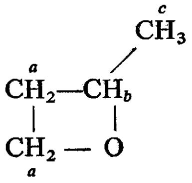
The rate of hydrogen abstraction by methyl radicals from an oxetan ring has not previously been measured and the Arrhenius parameters reported for hydrogen abstraction from cyclic hydrocarbons generally show wide discrepancies. Comparison of the rate constants for H atom removal on a per-atom basis at a median temperature (in table 3) shows, however, that the hydrogens of methylene groups in

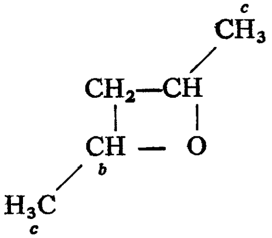
TABLE 3.—COMPARISON OF RATE PARAMETERS FOR HYDROGEN ABSTRACTION

substrate	$\log_{10}(A$ $/\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	$E/\text{kJ mol}^{-1}$	$\log_{10}(k_{164^\circ\text{C}}$ $/\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	ref.
	11.0	43.1	5.07	10
	11.1	42.7	5.22	11
	11.7	54.8	4.38	12
	11.0	40.2	5.59	11
	10.4	37.7	5.29	13
	11.4	38.9	5.85	10
	12.18	42.3	6.22	14
	11.3	35.2	6.31	this work
$CH_3CH_2CH_3$	11.82	42.4	6.46	15
CH_3CH_2OH	11.60	40.5	6.46	9

oxygenated rings appear to be more labile than those in the corresponding cyclic hydrocarbons. In contrast, the hydrogen atoms of the methylene group in propane appear to be similar to those in the methylene group of ethanol. In view of the similarity between the *A*-factors for the corresponding pairs of compounds it is clear that the increased lability is primarily due to the lowered activation energy for the oxygenated ring compounds. If it is assumed that all the hydrogen atoms in oxetan are equivalent, then three different types of H atom can be distinguished in the three compounds studied. These may be labelled *a*, *b* and *c* as below and the rate constants for their abstraction denoted by k_a, k_b and k_c.







Assuming that the rate constants are additive, the total rate constants for hydrogen abstraction are given by

$$k_{4(\mathrm{ox})} = 6k_a$$

$$k_{4(2\mathrm{ox})} = 4k_a + k_b + 3k_c$$

$$k_{4(2,4\mathrm{ox})} = 2k_a + 2k_b + 6k_c.$$

From these relationships it is clear that

$$k_{(2\mathrm{ox})} = [k_{(\mathrm{ox})} + k_{(2,4\mathrm{ox})}]/2$$

and this is shown to be true, within experimental error, from the data in table 4.

TABLE 4.—TEST OF RATE CONSTANT RELATIONSHIP

T/°C	$[k_{\mathrm{ox}} + k_{(2,4\mathrm{ox})}]$ /10^6 cm^3 mol^{-1} s^{-1}	$2k_{2\mathrm{ox}}$ /10^6 cm^3 mol^{-1} s^{-1}
100	8.90	9.04
150	32.4	33.1
200	89.9	91.8

Since these equations are not sufficient to solve explicitly for k_a, k_b and k_c, the relative rates of attack at various positions can only be found by making a further assumption. The rate of abstraction of H atoms in the side chain is likely to be low and may be taken to be similar to that for H abstraction from a methyl group in propane. Using the parameters $\log_{10}$ (A/cm^3 mol^{-1} s^{-1}) = 12.04 and E/kJ mol^{-1} = 48.2 reported [12] for overall H abstraction from primary C—H bonds in propane we have calculated k_c at each of our experimental temperatures and then used the relationships above to find the Arrhenius parameters for k_a and k_b. The results yield

$$\log_{10} (A_a/\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 10.51,\ E_a/\mathrm{kJ\ mol^{-1}} = 35.2$$

$$\log_{10} (A_b/\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 11.0,\ E_b/\mathrm{kJ\ mol^{-1}} = 32.4.$$

These figures show that at a temperature of 164°C (close to the middle of the experimental range) the relative rate of attack at site b compared with site a is given by

$$k_b/k_a \approx 6.7.$$

This result is in accord with expectations based on estimated bond dissociation energies for secondary and tertiary H-atoms in these ring compounds. It could also explain the fact that small amounts of minor products such as methane and ethane are often found in the thermolysis products of mono-alkyl-substituted oxetans [1] and that while small, these amounts are larger than can be detected in the thermolysis of unsubstituted oxetan.[16] The differences, both kinetic and in relation to minor products, which are noted between the thermolyses of 2- and 3-alkyl-substituted oxetans may indicate a difference in reactivity between tertiary H atoms located near to or remote from the ring oxygen atom. Further work is in progress to investigate this possibility by studying abstraction from a wider range of methyl-substituted oxetans.

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