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Chemical Activation Study of the Reactions of Methylene with Oxetan and 3,3-Dimethyloxetan

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Methylene (singlet) formed by the photolysis of ketene (313 nm) reacts with oxetan to yield 2-methyl- and 3-methyloxetans by insertion in the C—H bonds and probably also tetrahydrofuran. These products are formed chemically activated and undergo unimolecular decomposition unless collisionally stabilized. Using perfluoropropane as the bath gas, the results obtained with 2-methyloxetan have been interpreted using RRKM theory and a step-ladder model with a most probable step size of *ca.* 9 kJ mol^{-1}. Using 206 nm radiation yields methylene with excess energy, some of which is still present when it reacts, and results in the production of 2-methyloxetan with an average lifetime approximately one-half that of the energised molecule produced when 313 nm radiation is used.

Similarly methylene reacts with 3,3-dimethyloxetan to yield chemically activated 3-ethyl-3-methyloxetan and 2,3,3-trimethyloxetan. A third compound tentatively identified as 3,3-dimethyltetrahydrofuran is also formed. The decomposition of these 3 molecules has been followed and in the case of the ethylmethyloxetan the average energy transferred in collision with 3,3-dimethyloxetan has been found to be *ca.* 6.5 kJ mol^{-1}.

Some deductions can be made about the Arrhenius parameters for the thermal decomposition of the (as yet unreported) trimethyloxetan and the dimethyltetrahydrofuran.

In the past two decades there have been many studies of chemically activated sytems produced by the addition of methylene to hydrocarbons.[1-6] In the main, the activated molecules have been cyclopropanes, produced by the addition of methylene to olefins or cyclobutanes produced by methylene insertion reactions. In the present work we present the first study of this type involving the oxetan ring system.

EXPERIMENTAL

MATERIALS

Oxetan and 3,3-dimethyloxetan were commercial samples. They were purified to better than 99.9% by preparative gas chromatography using a 2 m silicone oil column. Cyclohexane, used as an internal standard, was purified similarly. Perfluoropropane (99%) was obtained from Matheson and was further purified by several trap-to-trap distillations. Ketene was prepared by the pyrolysis of acetic anhydride and purified by trap-to-trap distillation at −80 °C to remove a small ethylene impurity.

APPARATUS

A conventional high-vacuum system equipped with Teflon/glass stopcocks was employed. Photolyses were carried out using a medium-pressure mercury lamp (Hanovia UVS 500) and a Pyrex reaction vessel or using an iodine lamp, powered by a microwave source (Microton 200), and a silica reaction vessel.

ANALYSIS

All quantitative analysis was carried out by gas chromatography using a Perkin-Elmer F11 instrument equipped with a gas sampling valve and a flame-ionization detector. Signals from the detector were recorded using a Hewlett–Packard 3380A integrator. To reduce adsorption problems the metal sample loops normally used were replaced by glass U tubes of 5 or 10 cm^3 volume which were wrapped in heating tape to maintain them at between 90 and 100 °C.

For studies using oxetan the analytical column was 2 m by 2.2 mm (i.d.) packed with di-2-ethylhexyl sebacate on 60/80 mesh Chromosorb P and operated at room temperature. For studies using 3,3-dimethyloxetan a similar column 4 m long was employed at 80 °C. Before each photolysis the reaction mixture was analysed and after photolysis analyses in duplicate were obtained.

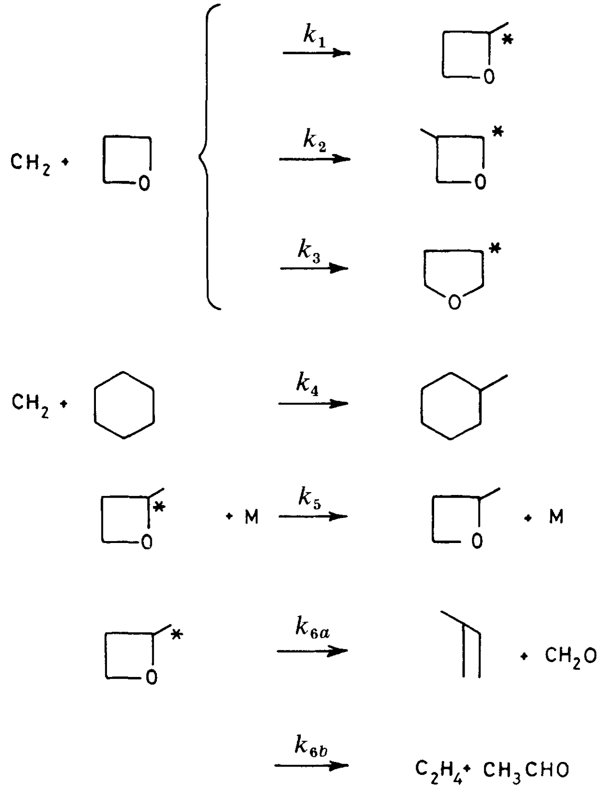
PROCEDURE

A mixture of ketene, oxygen, cyclohexane and oxetan (or dimethyloxetan) in the ratio 0.7:0.3:1:4 was prepared in the vacuum system. Samples of this mixture at various total pressures were photolysed at *ca.* 313 nm for 2 h or at 206.2 nm for 1 h and analysed immediately after photolysis. For total pressures above 55 Torr, 54 Torr of the mixture was used and perfluoropropane added to the required pressure.†

RESULTS

OXETAN SYSTEM

In the presence of oxygen, triplet methylene and any radical products react rapidly and were not detected in our analysis. The products that are observed are those resulting directly or indirectly from singlet methylene reactions. The following reactions were expected to occur, based on analogies with other methylene systems and the thermal studies on the decomposition of alkyl oxetans.[7-9]



(1)

(2)

(3)

(4)

(5)

(6*a*)

(6*b*)

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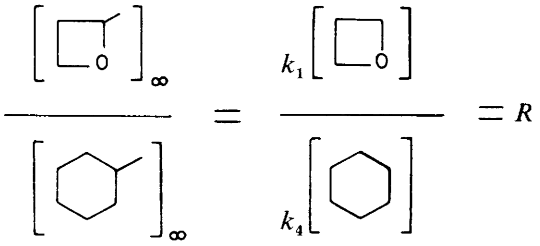
† 1 Torr = (101 325/760) Pa.

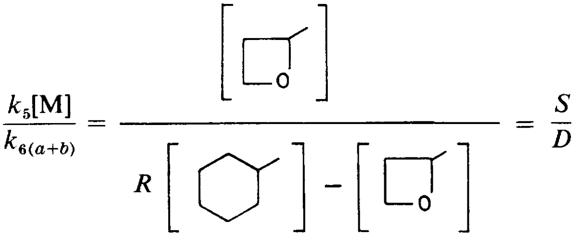
An asterisk indicates a vibrationally excited molecule which contains sufficient energy to undergo unimolecular decomposition. The fate of such a molecule is either to be collisionally stabilised as depicted in reaction (5) or decompose as indicated by reaction (6). There will, of course, be analogous reactions for the products that are produced by reactions (2) and (3) but for reasons that will emerge they do not concern us in the present work. Under all the experimental conditions employed, methylcyclohexane can be considered as completely stable and thus its yield can be used as a monitor of the total singlet methylene introduced into the system.

At high pressures when $k_5[\mathrm{M}] \gg k_6$ it is easy to show that



(I)

and the value of R was obtained experimentally by extrapolation. Hence it can be seen that at lower pressures



(II)

where S and D refer to the 2-methyloxetan molecules that are stabilized (by collision) or undergo unimolecular decomposition, respectively.

The use of an internal standard (cyclohexane) was necessary since the alternative method of determining the variation of S/D with pressure would have required the measurement of the propene or formaldehyde produced by reaction (6*a*). There are several problems associated with such determinations. First, these products are also formed from the decomposition of vibrationally excited tetrahydrofuran and 3-methyloxetan. In addition, formaldehyde is difficult to determine quantitatively and propene is always present in methylene systems, formed from the addition of methylene to ethylene (itself coming from the reaction of methylene with ketene). Similar considerations apply to the determination of ethylene formed by reaction (6*b*).

In principle, it should be possible to determine the variation of S/D with pressure for 3-methyloxetan and tetrahydrofuran by exactly the same method employed for the 2-methyloxetan. In the present work that was not found to be possible since despite considerable effort we could not find a suitable chromatographic column which would separate the two oxetans, tetrahydrofuran, cyclohexane, methylcyclohexane and two impurity peaks. With the column finally selected, 3-methyloxetan and tetrahydrofuran co-eluted.

Measurements of S/D values as a function of pressure were obtained for vibrationally excited 2-methyloxetan produced using 313 nm light. The pressure range covered was from *ca.* 10 to *ca.* 1500 Torr. For most of the experiments the bulk of the reaction mixture was perfluoropropane. At low pressures corresponding to values of S/D below 0.2 the data were not very reproducible and the values did not extrapolate to zero at zero pressure as expected. We believe that a small impurity together with a secondary photolysis product which co-eluted with the methyloxetan were responsible for these findings. Some confirmation for our hypothesis was obtained by using a 6 m chromatographic column in place of the usual 2 m column, when a 'shoulder' was observed on the peak. We have, therefore, restricted our discussion to values of S/D in the range from *ca.* 0.3 to > 10.

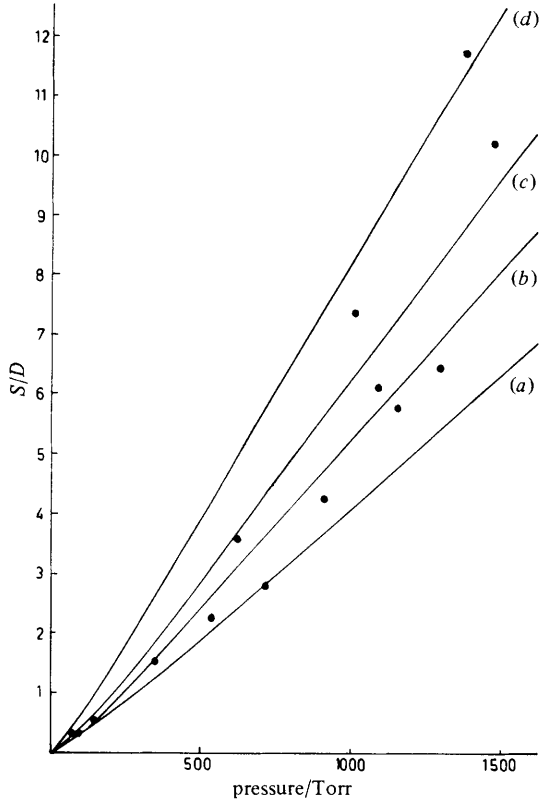


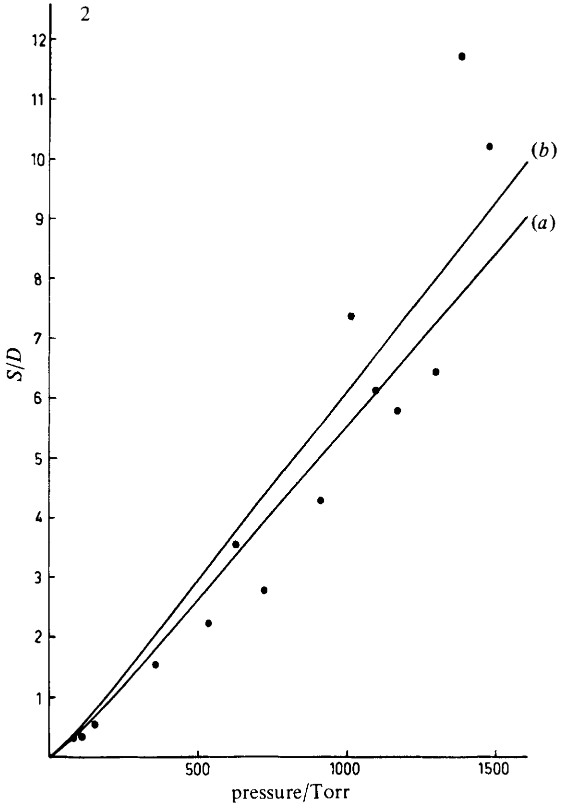
FIG. 1.—Decomposition of activated 2-methyloxetan. Experimental points from ketene (313 nm) + oxetan. Theoretical lines assume $E = 448$ kJ mol^{-1}, σ (2-methyloxetan) = 5.5 Å. (*a*) $\Delta E = 7.2$ kJ mol^{-1}, (*b*) $\Delta E = 8.4$ kJ mol^{-1}, (*c*) $\Delta E = 9.6$ kJ mol^{-1}, (*d*) $\Delta E = 12.0$ kJ mol^{-1}.

The experimental results are shown in fig. 1 and 2. The theoretical curves that are drawn will be discussed later.

In a second series of experiments, S/D values were determined using an iodine lamp as the photolysis source (206 nm). At any particular pressure the value of S/D was smaller in this series than when the 313 nm light source was used. Runs covered a pressure range from 100 to 900 Torr and values of S/D ranged from 0.2 to 3.2. The results obtained are shown in fig. 3.

3,3-DIMETHYLOXETAN SYSTEM

A preliminary set of photolyses at 313 nm using a mixture of ketene, oxygen and 3,3-dimethyloxetan showed 3 product peaks with longer retention times than the



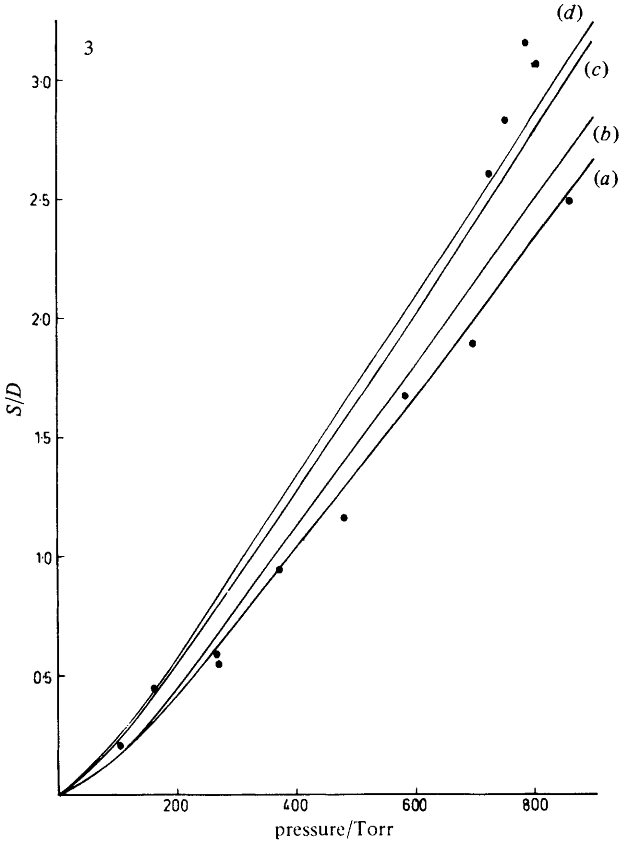
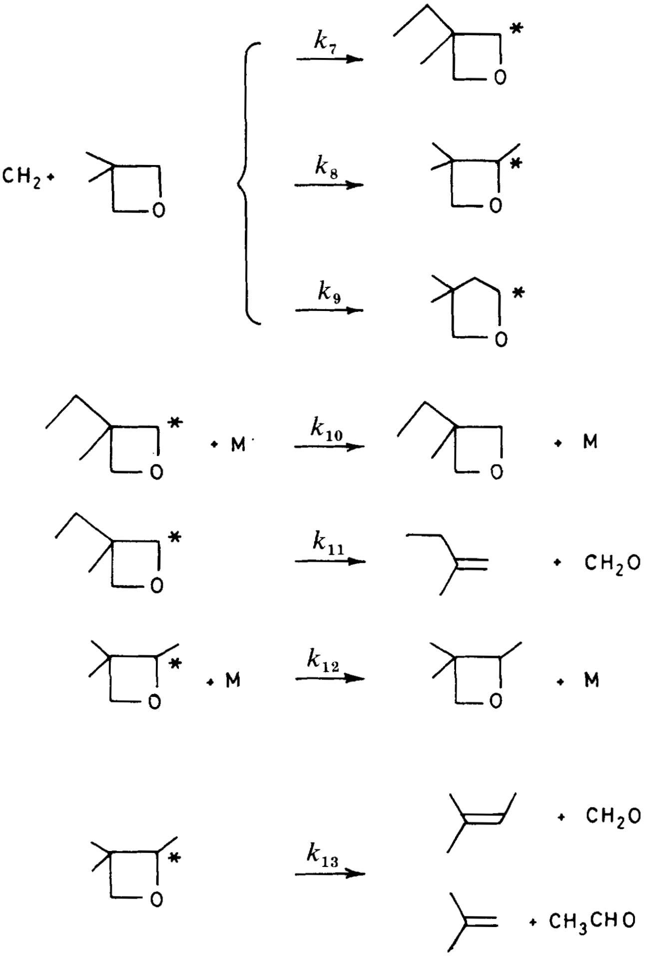


FIG. 2.—Decomposition of activated 2-methyloxetan. Experimental points ketene (313 nm)+oxetan. Theoretical lines assume $E = 481$ kJ mol^{-1} and $\Delta E = 30$ kJ mol^{-1}. (*a*) σ (2-methyloxetan) = 5.5 Å, (*b*) σ (2-methyloxetan) = 6.0 Å.

FIG. 3.—Decomposition of activated 2-methyloxetan. Experimental points ketene (206 nm)+oxetan. Theoretical lines assume $E = 502$ kJ mol^{-1}. (*a*) $\sigma = 6.0$ Å, $\Delta E = 24$ kJ mol^{-1}, (*b*) $\sigma = 5.5$ Å, $\Delta E = 30$ kJ mol^{-1}, (*c*) $\sigma = 6.0$ Å, $\Delta E = 30$ kJ mol^{-1}, (*d*) $\sigma = 5.5$ Å, $\Delta E = 36$ kJ mol^{-1}.

reactant oxetan. The product with the longest retention time was identified as 3-ethyl-3-methyloxetan by comparison with an authentic sample. The other two products, which were not completely resolved from one another, were assumed to be 2,3,3-trimethyloxetan and 3,3-dimethyltetrahydrofuran. Many peaks with retention times less than the reactant oxetan were observed and were identified as including ethylene, propene, allene, isobutene, 1,1-dimethylcyclopropane, 2-methylbut-1-ene and 2-methylbut-2-ene.

Again, by analogy with other systems[10] we expect the observed products to result from singlet methylene reactions as follows.



(7)
(8)
(9)
(10)
(11)
(12)
(13*a*)
(13*b*)

As with the oxetan system, so also with the 3,3-dimethyloxetan system a series of runs was carried out with a reaction mixture containing cyclohexane, once again using methylcyclohexane as a measure of the singlet methylene produced during the photolysis. In this manner it was possible to determine S/D values as a function of pressure for the 3-ethyl-3-methyloxetan (*i.e.* k_{10} [M]/k_{11}) as well as the corresponding values for k_{12}[M]/k_{13}.

The chromatographic peak ascribed to the dimethyltetrahydrofuran varied with pressure in a similar way to the oxetan peaks and hence we could determine S/D values for this compound.

Photolysis with total pressures in the range 1-36 Torr and using the 313 nm light source yielded the S/D values for the 3-ethyl-3-methyloxetan shown in fig. 4.

Similarly the corresponding values associated with 2,3,3-trimethyloxetan and 3,3-dimethyltetrahydrofuran are shown in fig. 5.

Some experiments were attempted using the iodine lamp. With this 206 nm source many more chromatographic peaks were produced than in the 313 nm experiments. A photolysis with the short-wavelength light of a reaction mixture of 3,3-dimethyloxetan, oxygen and cyclohexane but with no ketene gave these extra peaks, as well as some products that had the same retention times as the methylene addition products. It appears that there is sufficient 'end absorption' by the substituted oxetan at 206 nm to yield measurable decomposition products and so no further work was undertaken with this radiation.

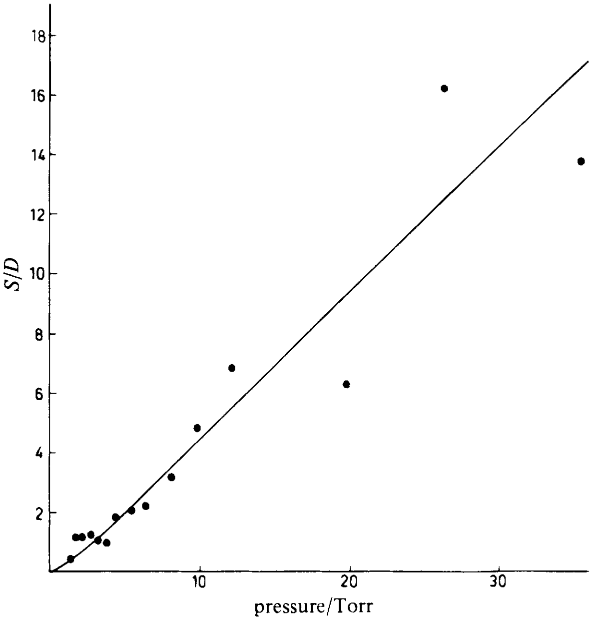


FIG. 4.—Decomposition of activated 3-ethyl-3-methyloxetan. Theoretical line, $E = 440$ kJ mol^{-1}, $\Delta E = 6.5$ kJ mol^{-1}.

DISCUSSION

OXETAN SYSTEM

As outlined in the Results section, experimental problems prevented the determination of S/D values for other than the vibrationally excited 2-methyloxetan. The experimental values obtained shown in fig. 1 are compared with theoretical calculations. The calculated curves were obtained by the application of RRKM theory using various models. We describe briefly the basis of these calculations.

To derive S/D values we need to evaluate k_5[M] and k_6. The evaluation of k_5[M] requires the assignment of collision diameters to the various molecules present in the reaction mixture and an assumption about the nature of the energy-transfer process. In much early work the strong collision hypothesis was employed, which is equivalent in the present work to equating k_5[M] directly to the collision frequency. A modification of the strong collision hypothesis is to accept that energy is exchanged

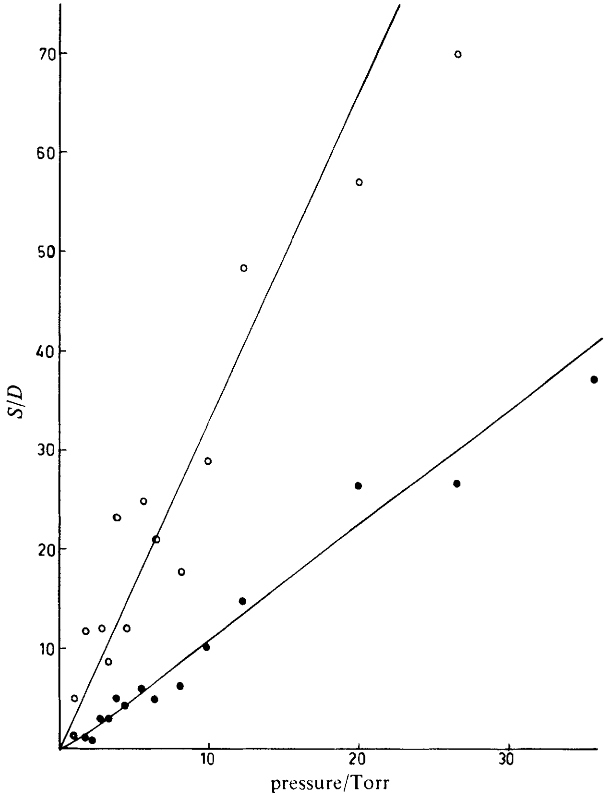
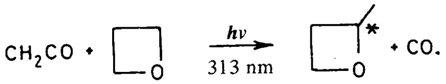


FIG. 5.—Decomposition of activated 2,3,3-trimethyloxetan and 3,3-dimethyltetrahydrofuran. ●, 2,2,3-trimethyloxetan; ○, 3,3-dimethyltetrahydrofuran.

in every collision of the energised molecule but that the amount transferred is not necessarily sufficient to result in deactivation. The simplest model of this kind is the 'step-ladder model' of Tardy and Rabinovitch[11] and we use it in the present work. Various possible step sizes can be tried using them as an adjustable parameter.

To evaluate k_6 a detailed structure must be assigned to the activated complex. This is carried out using whatever information is available from thermal studies *etc.* The structure of the complex must yield a value for the experimental entropy of activation, again available from conventional thermal studies. While these restrictions are minimal and in no sense define a unique complex, previous work has shown that provided the conditions that have been mentioned are satisfied, the numerical value of k_6 is not critically dependent on the fine details of the structure of the complex. Leading to greater uncertainty in the present work is the further requirement of specifying the total energy available in the energised molecule to which k_6 is indeed very sensitive. The minimum energy the energised 2-methyloxetan molecule can possess is given by the enthalpy change of reaction (1). We can evaluate this using group additivity to estimate the difference between the heats of formation of oxetan and 2-methyloxetan and the heat of formation of singlet methylene. This yields a value of 448 kJ mol^{-1} (107 kcal mol^{-1}) with an uncertainty of perhaps 15 kJ mol^{-1} largely arising from uncertainties in the heat of formation of singlet methylene. However, there is evidence from many other studies of species produced by chemical activation involving the addition or insertion reactions of singlet methylene that the methylene may contain excess energy related to its genesis and that this can be carried into the activated molecule.[12] We therefore also evaluate the maximum energy the vibrationally excited methyloxetan might contain by a calculation based on the ΔH_{298} for the reaction



On the assumption that the carbon monoxide is formed vibrationally 'cold', then the 2-methyloxetan could have as much as 475 kJ mol^{-1} (114 kcal mol^{-1}) excess energy. In our calculations we have obtained values for k_6 relating to a relatively wide range of initial energies to ensure that we covered all possible values including reasonable experimental uncertainties.

On the basis of the strong collision hypothesis the experimental magnitude of S/D at around the middle of the pressure range investigated ($S/D \approx 5$) yields a value for k_6 of between 1.7×10^9 and 1.9×10^9 s^{-1} (depending on a choice for the collision diameters for methyloxetan of 5.5 and 6.0 Å respectively. A collision diameter for C_3F_8 of 5.03 Å has been used throughout). With the model chosen (see Appendix) these values of k_6 correspond to an excess energy of between 501 and 508 kJ mol^{-1} (120-121 kcal mol^{-1}). These values are greater than the maximum possible, as discussed above. Since previous work has shown that even radical changes in the vibrational assignments of the activated complex have little effect on the values of $k(E)$, the variation of rate constant with energy, we must conclude that the strong collision hypothesis fails in the present study.

We have investigated the step-ladder (model) variant of the strong collision hypothesis. For an excess energy of 481 kJ mol^{-1} (115 kcal mol^{-1}) which is essentially the maximum possible energy that the 2-methyloxetan can have at the experimental temperature (350 K) and a collision diameter of 6 Å, a reasonable fit to the experimental data for S/D ratios below *ca.* 8 can be obtained with a step size (ΔE) of 24 kJ mol^{-1} (5.7 kcal mol^{-1}). The fit of the curve with $\Delta E = 30$ kJ mol^{-1} is very appreciably worse. We estimate the best fit would be with $\Delta E = 23$ kJ mol^{-1}. If the collision diameter of the 2-methyloxetan is reduced to the low value of 5.5 Å then $\Delta E = 30$ kJ mol^{-1} is a reasonable fit and we estimate $\Delta E = 27.5$ kJ mol^{-1} (6.5 kcal mol^{-1}) as the best fit.

Using an excess energy of 448 kJ mol^{-1} (107 kcal mol^{-1}), which is close to what we estimate as the most probable value, a reasonable fit is obtained with $\Delta E = 9.6$ kJ mol^{-1} (2.3 kcal mol^{-1}); this drops to $\Delta E = 8.4$ kJ mol^{-1} (2.0 kcal mol^{-1}) if the smaller collision diameter for 2-methyloxetan is used.

Within the accuracy of our results we are therefore only able to give a range of acceptable values for E and ΔE with the most probable values closer to the lower limits than the upper ones. It is also clear that above S/D values of *ca.* 7 the experimental points fall off all the theoretical curves. However, at high values the experimental errors can be very large and are mainly dependent on the magnitude chosen for the value of R [see eqn (I)]. The extrapolated value of R using a ratio of oxetan to cyclohexane of 1.5:1.0 was 0.50 ± 0.02. (It is interesting to note that this implies that the reactivity of singlet methylene towards the carbon–hydrogen bonds adjacent to the oxygen in oxetan and the carbon–hydrogen bonds in cyclohexane is identical. In many other systems the insertion of singlet methylene in various types of carbon–hydrogen bonds has shown almost no discrimination.) A change of only 4% in the value of R leads to the calculated value for S/D changing from 7.4 to 11.1 Even a 1% change in R leads to an increase to 8.1. For this reason we do not feel that the apparent deviation of the points at high values of S/D warrants further consideration.

The results obtained using 206 nm radiation as the photolytic source are similar to those with the 313 nm light, but at any particular pressure the S/D ratio is smaller for the shorter-wavelength radiation. This indicates that the initially formed 2-methyloxetan has a greater energy content which implies that some of the excess energy carried by the singlet methylene from its genesis is still present when it reacts. This is consistent with other studies and is a consequence of the high collision efficiency with which singlet methylene reacts.

Up to a total pressure of 700 Torr, corresponding to a value of S/D of *ca.* 2.0, the experimental results can be well fitted using a range of values of E and ΔE. If we assume that the value of ΔE is the same as for the slightly less energetic methyloxetan molecules produced from the 313 nm photolysis, then we may calculate an appropriate value of E. Thus if we take $\Delta E = 24$ kJ mol^{-1}, the corresponding value of E is 502 kJ mol^{-1} (120 kcal mol^{-1}), which yields the difference between the excess energy carried by the 2-methyloxetan produced by the different photolytic radiation as *ca.* 21 kJ mol^{-1}. Alternatively, if we select a value for ΔE of 9.6 kJ mol^{-1}, then the corresponding value of E is 461 kJ mol^{-1}, *i.e.* again a difference of 21 kJ mol^{-1}.

The deviation of the points from the calculated line at pressures above 700 Torr may in part be due to experimental error; certainly there is appreciable scatter. However, the effect may be real and would result if there was an energy spread in the initially produced energised molecules. This would not be unexpected if the singlet methylene did react while still having excess energy since the actual magnitude of this excess would depend not only on the initial photolytic step but also on the number of collisions suffered by a methylene radical before it underwent reaction. Finally, we note that the energy difference of 21 kJ mol^{-1} is scarcely more than 10% of the energy difference between a 313 and a 206 nm photon (*ca.* 200 kJ mol^{-1}).

3,3-DIMETHYLOXETAN SYSTEM

As discussed for the methylene–oxetan system, we calculate the most probable total energy of the various energised molecules by reference to the thermochemistry of their forming reactions. To a first approximation two of the energised species, *viz.* 3-ethyl-3-methyloxetan and 2,3,3-trimethyloxetan, will have similar excess energies. With 313 nm radiation we believe these will be close to 440 and 448 kJ mol^{-1}, respectively.

3-ETHYL-3-METHYLOXETAN

As before we can calculate the maximum possible energy that the energised molecule may possess as 472 kJ mol^{-1} and with this value use various values of ΔE to obtain a fit between theory and experiment. Reasonable agreement is obtained with $\Delta E \approx 17$ kJ mol^{-1} (4 kcal mol^{-1}).

In a similar fashion, if what we consider the much more probable value of $E = 440$ kJ mol^{-1} (105 kcal mol^{-1}) is used then a good fit is obtained with $\Delta E = 6.5$ kJ mol^{-1} (1.6 kcal mol^{-1}).

These values of ΔE are relatively small when compared with the results obtained in some other chemical activation systems. It is, however, interesting that the value of ΔE for the more complex energized molecule 3-ethyl-3-methyloxetan is smaller than that for the 2-methyloxetan. This trend has been commented on and rationalized for other systems.[12] It should be further noted that the energy transfer in this system is predominantly between the activated molecule and 3,3-dimethyloxetan rather than perfluoropropane. Since the fluorinated molecule is likely to be a less efficient collision partner the difference between the values of ΔE is noteworthy.

2,3,3-TRIMETHYLOXETAN

To date no thermal kinetic studies have been reported on this compound. In the absence of Arrhenius parameters for the decomposition we are unable to carry out detailed RRKM calculations to fit our experimental data.

From the variation of S/D with pressure for the trimethyl compound compared with the ethylmethyloxetan, we may deduce that provided that 'A' factors for the two decompositions do not differ appreciably (and evidence from other oxetan studies supports this) then the former compound will have the higher energy of activation. As we have already noted, RRKM calculations are not very sensitive to the detailed 'structure' of the activated complex so it is possible to estimate the energy of activation for the trimethyloxetan based on the present data and the thermal data for the 3-ethyl-3-methyloxetan. Our calculations yield a value for the energy of activation for the decomposition of the 2,3,3-trimethyloxetan of 258.5 kJ mol^{-1} (61.8 kcal mol^{-1}) which is 7.5 kJ mol^{-1} higher than that for the ethylmethyloxetan. This leads to a prediction that at around 450 °C the 2,3,3-trimethyloxetan will decompose *ca.* 0.56 times as fast as 3-ethyl-3-methyloxetan. For these comparisons we have used $E = 448$ kJ mol^{-1} and $\Delta E = 6.5$ kJ mol^{-1}.

3,3-DIMETHYLTETRAHYDROFURAN

The identification of this compound must be considered provisional. It is based on the earlier report of carbon–oxygen bond insertion reactions of methylene and in particular the observation that in its gas phase reaction of singlet methylene with tetrahydrofuran relatively large yields of tetrahydropyran were obtained.[14] (A solution study has shown that carbethoxycarbene reacts with a phenyloxetan to yield a substituted tetrahydrofuran.[15])

If 3,3-dimethyltetrahydrofuran is indeed formed then we calculate it will have a most probable excess energy of *ca.* 522 kJ mol^{-1} (125 kcal mol^{-1}). Despite this very large excess energy compared with that carried by the chemically activated 3-ethyl-3-methyloxetan (the difference largely reflects the difference in the strain energies of the 4 and 5 membered rings), the excited molecule undergoes decomposition at a rate some 7 times slower than the oxetan. This must reflect a much higher energy of activation for the decomposition of tetrahydrofurans compared with oxetan which is not at all unexpected. No useful data appear to be available from conventional thermal studies on tetrahydrofurans but a study on the shock-tube pyrolysis of cyclopentane does allow an estimate to be made of the order of magnitude of the parameters involved. Tsang[16] showed that cyclopentane decomposed by two pathways to give initially pent-1-ene and cyclopropane and ethylene. The energy of activation of the first pathway, 355 kJ mol^{-1} (84.9 kcal mol^{-1}), suggests the breaking of a C—C bond to give the pentamethylene biradical followed by a hydrogen-transfer step which must have a relatively high energy barrier. (The pathway yielding cyclopropane and ethylene has an even higher energy of activation.) The decomposition of the substituted tetrahydrofuran must almost certainly follow similar pathways. Because the 3,3-dimethyltetrahydrofuran has a tertiary centre we would expect the initial bond rupture to occur with an energy of activation between 17 and 20 kJ mol^{-1} less than in the case of cyclopentane. It is also possible that the hydrogen-transfer step has a lower energy of activation in the oxygen-containing biradical than in pentamethylene. Hence we might expect an energy of activation of around 335 kJ mol^{-1} or a little less. RRKM calculations of exactly the same kind as carried out for the other chemically activated molecules produced in this work yielded a set of A factors and corresponding values of E_a which gave a value of $k(E)$ consistent with the experimental results. If log A/s^{-1} is taken as 16.4 then the corresponding value of E_a is 320 kJ mol^{-1}. Both of these parameters seem very reasonable. (Note that if a slightly higher A factor is selected there is a corresponding increase in E_a, *e.g.* log $A/s^{-1} = 17$ then $E_a = 340$ kJ mol^{-1}.) Thus this study yields the prediction that tetrahydrofurans are likely to decompose in a similar way to cyclopentanes but with slightly lower energies of activation.

APPENDIX

RRKM CALCULATIONS

Vibrational assignments (cm^{-1}), degeneracies in brackets where appropriate.

2-METHYLOXETAN

Energised Molecule

2947 (8), 1449 (5), 1304 (4), 1150 (3), 1021, 1012 (4), 923 (2), 838, 680, 400, 350 (2), 182.

Activated Complex

2947 (8), 1449 (5), 1304 (4), 1150 (3), 1012 (4), 923, 680, 400 (2), 350 (2), 345, 95.

Path degeneracy 4. Ratio of rotational partition functions taken as unity. $E_a = 248.1$ kJ mol^{-1}.

Note: The assignments given above were based on the Arrhenius parameters reported in ref. (7); these are also close to those reported for 2-ethyloxetan in ref. (8). Since our work has been completed, slightly higher parameters have been reported in ref. (9). We do not believe the small differences involved warrant a re-evaluation of our calculations. Also, the decomposition occurs by two pathways each with its own activated complex and each with a path degeneracy of 2. Since we were unable to separate these in our work we have chosen a 'composite' complex with a path degeneracy of 4.

3-ETHYL-3-METHYLOXETAN ENERGISED MOLECULE

2947 (8), 2916 (4), 1451 (7), 1363 (2), 1304 (4), 1285, 1245, 1150 (3), 1021, 1012 (4), 973 (3), 923 (2), 838, 739, 680, 447, 400, 350 (2), 213, 195, 182, 101.

Activated Complex

2947 (8), 2916 (4), 1451 (7), 1363 (2), 1304 (4), 1285, 1245, 1150 (3), 1012 (4). 973 (3), 923, 739, 680, 447, 400, 350 (2), 300, 285, 213, 195, 101, 60.

Path degeneracy 4. Ratio of rotational partition functions taken as unity. $E_a = 251.2$ kJ mol^{-1}.

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