# 570. *The Photolysis of 3-t-Butyldiazirine*

By H. M. Frey and I. D. R. Stevens

The photolysis of 3-t-butyldiazirine has been investigated in the gas phase in the pressure range 0·5—82 mm. The photolysis has also been carried out in the presence of added ethylene and propylene to a total pressure of over 1000 mm. At high pressures, the photolysis produces roughly equal amounts of 1,1-dimethylcyclopropane and 2-methylbut-2-ene. At low pressures, the yield of the cyclopropane decreases, that of the 2-methylbut-2-ene increases, and a new product, 3-methylbut-1-ene, is formed. At the lowest pressures investigated, small quantities of 2-methylbut-1-ene were detected. The results are explained in terms of a mechanism involving three primary processes, one to give 2-methylbut-2-ene, and the second to give 1,1-dimethylcyclopropane, which is stable, and the third, 1,1-dimethylcyclopropane which is vibrationally excited and contains sufficient energy to isomerise to olefins unless collisionally stabilised. This third path may involve the intermediacy of a carbene. Results are also reported on the pyrolysis of the diazirine.

THE photolysis of various diazirines has been undertaken to investigate the reactions of carbenes in the gas phase, and also to determine the properties of the highly vibrationally excited molecules that are formed.[1-3] So far, except in the case of diazirine itself,[4] conclusive evidence for the intermediate formation of a carbene has not been obtained. The present work was undertaken to extend our knowledge of these systems. In particular, it was to be expected that if the photolysis of the t-butyldiazirine produced t-butylcarbene, then this should undergo a highly characteristic reaction of carbenes, to yield a cyclopropane by an intramolecular insertion reaction.

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[1] H. M. Frey and I. D. R. Stevens, *J. Amer. Chem. Soc.*, 1962, **84**, 2647.
[2] H. M. Frey and I. D. R. Stevens, *J.*, 1963, 3514.
[3] H. M. Frey and I. D. R. Stevens, *J.*, 1964, 4700.
[4] H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 1962, 79.

## EXPERIMENTAL

*Preparation.*—3,3′,5-Tri-t-butyldiaziridino(1′,2′:1,2)-1,2,4-triazolidine (I), m. p. 92—95°, was prepared from 10N-methanolic ammonia, t-butyl hypochlorite, and pivalic aldehyde, using the method described by Schmitz [5] for the n-propyl analogue.

3-t-Butyldiazirine was prepared by adding a suspension of (I) in dilute sulphuric acid to an excess of sodium dichromate in dilute sulphuric acid at 40°. The reaction mixture was warmed to 60° and the diazirine swept out in a stream of nitrogen and condensed in a trap cooled in solid carbon dioxide. The crude diazirine was freed from pivalic aldehyde by repeated bubbling through saturated sodium hydrogen sulphite solution, dried over potassium hydroxide pellets, and collected at −78° as a colourless mobile liquid. It had infrared peaks at 1600 and 1000 cm.$^{-1}$, characteristic of the diazirine ring.

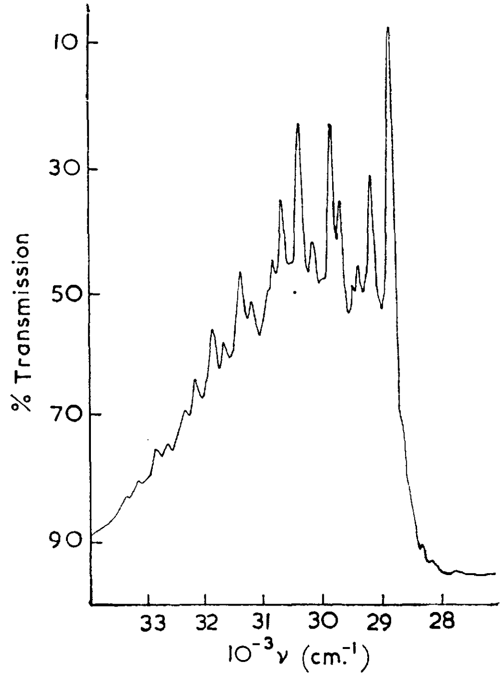

FIGURE 1. Ultraviolet absorption spectrum of t-butyldiazirine
"x" axis $10^{-3}$ frequency (cm.$^{-1}$).
"y" axis % transmission.

*Ultraviolet Spectrum.*—The ultraviolet spectrum is similar to those of other diazirines. Figure 1 shows the long-wavelength band (10-cm. gas-cell; 7 mm. pressure). The series of well-defined maxima extend from *ca.* 300 mμ (33,000 cm.$^{-1}$) to the highest maximum at 346 mμ (28,900 cm.$^{-1}$), $\varepsilon \sim 290$, with a sharp fall-off thereafter.

*Apparatus.*—A conventional high-vacuum apparatus was used for preparing all mixtures for photolysis and for the various gas-transfer operations. Greaseless stopcocks with Viton A diaphragms were used throughout to minimise absorption problems associated with the use of conventional greased stopcocks. Photolyses were carried out in cylindrical Pyrex vessels of various sizes, using the unfiltered radiation from a medium-pressure mercury arc (Hanovia U.V.S. 500). For work at the lowest pressures, a small trap was sealed on to the reaction vessel and isolated from it by a greaseless stopcock. After photolysis, the reaction mixture was frozen into this trap, prior to transfer to the analytical system.

*Analysis.*—Gas chromatography was employed. A 20-ft. column packed with 40/60 mesh Chromosorb P containing 20% w/w of di-2-cyanoethyl ether was followed by a short column (18 in.) packed with the same support containing 20% w/w of ethylene glycol saturated with silver nitrate. The columns were maintained at 0°. Hydrogen was the flow-gas and the detector was a Gow–Mac tungsten-filament katharometer in a conventional Wheatstone-bridge network. Signals were fed *via* a variable attenuator to a 1 mv recorder, and were integrated

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[5] E. Schmitz, *Chem. Ber.*, 1962, **95**, 688.

electronically (Perkin-Elmer model 194b). The inlet system to the chromatograph employed a multi-way gas-sampling valve (F and M model GV-11) with a stainless-steel sample volume, evacuated by a rotary pump. Products were identified in the first instance by comparison of their retention times with those of known compounds (either obtained commercially or synthesised during this work). Later, individual chromatographic peaks were trapped and analysed by mass spectrometry (A.E.I.—M.S. 3). Calibration factors were determined by the analysis of standard mixtures.

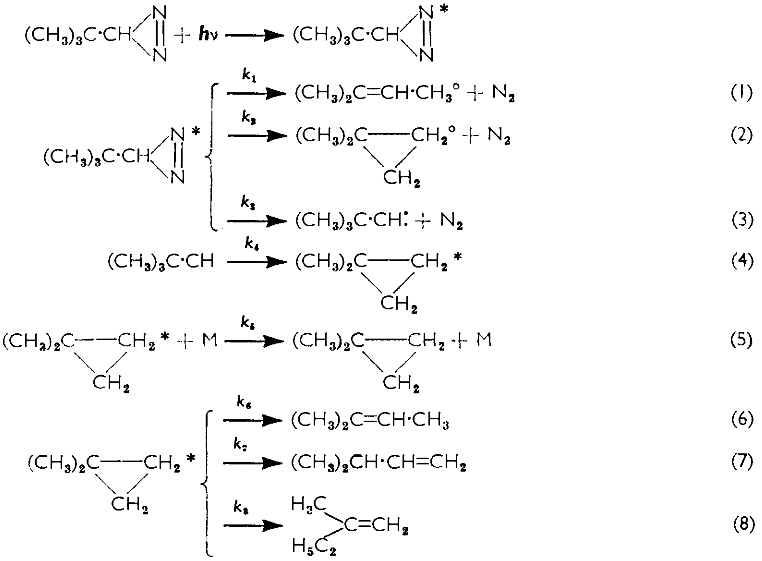
## RESULTS AND DISCUSSION

Photolyses were carried out in Pyrex reaction vessels whose volumes ranged from 20 to 600 ml. Results obtained at 15 and 65° were identical within experimental error. Accordingly, no attempt was made in the majority of runs to control the temperature, other than to ensure that it did not exceed 65°. In a series of runs with an initial pressure of t-butyldiazirine of 30 mm., the photolysis time was varied so that the decomposition covered the range 15—95%. The relative ratios of products were found to be quite insensitive to the percentage decomposition in this range. In the majority of runs, therefore, photolysis was allowed to continue until at least 80% of the diazirine had reacted.

Runs were carried out with initial pressures of t-butyldiazirine in the range 0·5—80 mm. Generally, after photolysis, the reaction mixture was passed directly into the evacuated sample volume of the gas chromatograph. However, for runs below 10 mm., the reaction mixture was frozen into a small trap cooled in liquid nitrogen, any non-condensable gas (essentially nitrogen) being removed by pumping. The mixture was then flash-evaporated and sampled directly from the trap. Most reaction mixtures were analysed in duplicate.

No attempt was made to filter the light from the mercury arc. With the medium-pressure mercury arc and a Pyrex reaction vessel, the only " active " radiation is that at 3130 and 3340 Å (31,950 and 29,940 cm.$^{-1}$, respectively).

As a result of the previous work with diazirines [1-4] and studies of vibrationally excited molecules produced by methylene reactions,[6] together with product analyses which will be reported in this Paper, the following mechanism is suggested, as a basis for discussion, to account for the major products from the photolysis of t-butyldiazirine: †



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† An asterisk * indicates a molecule or radical formed initially with sufficient energy to decompose. ° indicates a molecule, which while it may be vibrationally highly excited, does not possess sufficient energy to decompose.

[6] H. M. Frey, *Proc. Roy. Soc.*, 1959, *A*, **250**, 409.

At sufficiently high pressures, the only products should be 1,1-dimethylcyclopropane, 2-methylbut-2-ene, and nitrogen. With the pure diazirine at 81·5 mm., some 4% of 3-methylbut-1-ene was still produced. However, photolysis of 48 mm. of t-butyldiazirine in the presence of 1050 mm. of propylene yielded only 1,1-dimethylcyclopropane and 2-methylbut-2-ene (+ nitrogen) with only 0·4% of 3-methylbut-1-ene. The yields of the major hydrocarbon products as a function of pressure (at pressures below 42 mm.) are shown in Figures 2 and 3. The limiting yield of 2-methylbut-2-ene at high pressures can be found by extrapolation of the plot of the yield of this compound against the reciprocal of the pressure. This gives a value of 49% with an uncertainty of ±1%. This value is in close agreement with that obtained from the photolysis of t-butyldiazirine in the presence of a high pressure of propylene, when allowance is made for the small residual amount of isomerisation of the 1,1-dimethylcyclopropane.

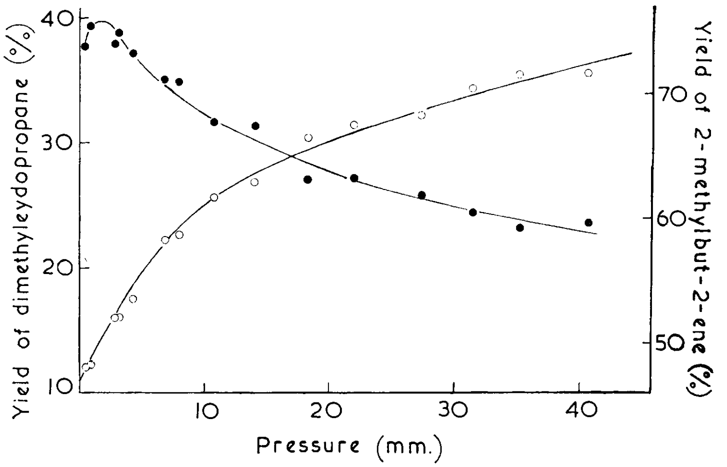

FIGURE 2. Yields of hydrocarbons as a function of pressure
○ 1,1-Dimethylcyclopropane. ● 2-Methylbut-2-ene.

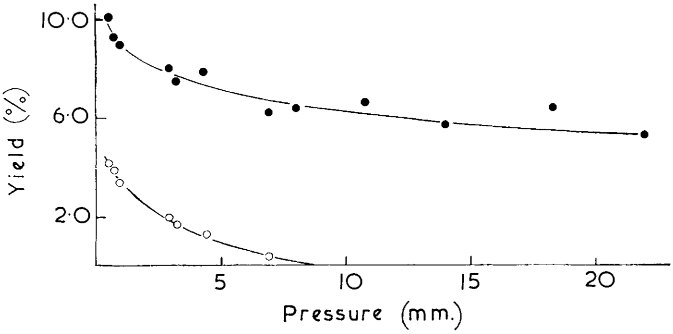

FIGURE 3. Yields of hydrocarbons as a function of pressure
○ 2-Methylbut-1-ene. ● 3-Methylbut-1-ene.

In a similar fashion, the yield of 1,1-dimethylcyclopropane formed by reaction 2 can be found by extrapolation to zero pressure of the plot of the total yield of the cyclopropane against pressure. Below about 10 mm., this plot is virtually linear and gives an extrapolated value of 11·3%.

An alternative procedure for obtaining the relative value of $k_2$, which does not require such careful extrapolation, is by consideration of the suggested mechanism. A stationary-state treatment of equations (1)—(8) yields the relationship:

$$\frac{[\text{Total yield of hydrocarbons}]}{[\text{Yield of isomerisation products}]} = \left(\frac{k_1 + k_2 + k_3}{k_3}\right)\left(1 + \frac{k_5\text{M}}{k_6 + k_7 + k_8}\right) \qquad (9)$$

If M is taken to be proportional to the initial pressure of the t-butyldiazirine (although the pressure will vary during the course of a photolysis, it has already been shown that the composition of the products is relatively insensitive to the percentage decomposition and hence to this factor), then a plot of the L.H.S. of equation 9 against pressure should yield a straight line with an intercept of $(k_1 + k_2 + k_3)/k_3$. To determine the yield of isomerisation products, we subtract from the total yield of 2-methylbut-2-ene, 3-methylbut-1-ene, and 2-methylbut-1-ene, the extrapolated yield of 2-methylbut-2-ene at high pressure (49%). A plot of the L.H.S. of equation 9 against pressure is shown in Figure 4.

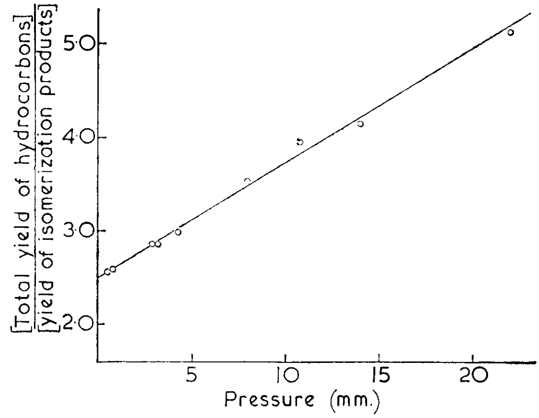

FIGURE 4. Ratio of total yield of hydrocarbon to isomerisation products, as a function of pressure

The plot obtained shows some curvature (which will be discussed later), but is linear at pressures below 20 mm. and extrapolates to a value at zero pressure of 2·5. This leads to the ratios $k_1 : k_2 : k_3$ being 0·49 : 0·11 : 0·40. Thus, the yield of 1-dimethylcyclopropane formed by reaction 2 is found to be 11%, in good agreement with the value obtained by direct extrapolation. Further, since this second procedure involves the value of the high-pressure yield of 2-methylbut-2-ene, whereas the former method does not, the agreement obtained gives support for both the magnitude of the yield of 2-methylbut-2-ene and also the suggested mechanism.

Some preliminary experiments on the pyrolysis of t-butyldiazirine indicate that the decomposition is a homogeneous first-order reaction. The only observed products were 1,1-dimethylcyclopropane, 2-methylbut-2-ene, and nitrogen. The yields of the hydrocarbon products were 92 and 8%, respectively. These values are in poor agreement with those of 80 and 20% quoted by Schmitz *et al.*[7] In general, the products and product ratios obtained from the pyrolysis of diazirines are very similar to those obtained by treatment of the corresponding tosylhydrazones with base in an aprotic medium. We note that the reaction of sodium methoxide with the tosylhydrazone of pivalic aldehyde is reported to yield[8] 1,1-dimethylcyclopropane, 2-methylbut-2-ene, and 2-methylbut-1-ene in yields of 92, 7, and 1%. These figures are closely similar to the values reported here and offer support for them.

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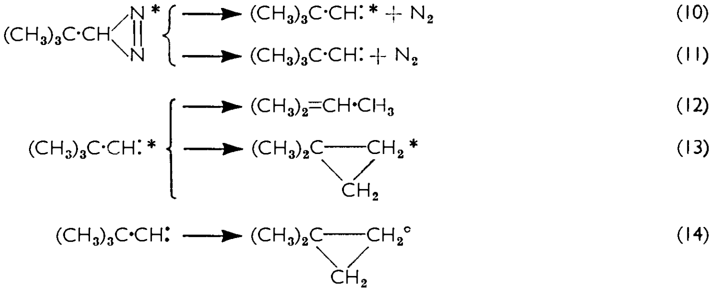
[7] E. Schmitz, D. Habish, and A. Stark, *Angew. Chem.*, 1963, **75**, 723.

[8] L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, 1959, **81**, 5512.

We have chosen, in the reaction mechanism, to consider the formation of the 1,1-dimethylcyclopropane by two distinct paths. The 1,1-dimethylcyclopropane formed by path (2) does not have sufficient energy to isomerise under our experimental conditions (*i.e.*, it contains less than *ca.* 70 kcal./mole energy). If this does occur in one step from the excited molecule of the diazirine, then the nitrogen molecule must carry a large fraction of the available energy. The formation of the 1,1-dimethylcyclopropane with enough energy to isomerise is postulated as occurring *via* the t-butylcarbene. We have no direct evidence for the intermediacy of this radical. Experiments carried out in the presence of large excesses of ethylene and propylene did not lead to the formation of any products which could be ascribed to addition reactions of the carbene. This is not too surprising, however, since, while methylene itself is highly reactive, methylcarbene (ethylidene) has been found to be far less reactive [9,10] and dimethylcarbene has not been found to undergo addition reactions. The evidence for the formation of the carbene is indirect and rests entirely on the similarity of the present system (and also the similar situations in work on the photolysis of other diazirines) to analogous systems involving normal diazo-compounds (either directly or as postulated intermediates) where the occurrence of carbenes has been assumed.[11] The absence of reactivity in the substituted carbene may be due to a higher energy of activation of the addition reactions compared with methylene itself, or to $k_4$ being very large, or to a combination of the two factors. In a similar fashion, we suggest that some 2-methylbut-2-ene is formed directly from the excited molecule of the diazirine [reaction (1)].

Exactly the same kinetics would result as long as one postulated the decomposition of the excited t-butyldiazirine to yield (with the resulting molecules having two sets of energy contents) the dimethylcyclopropane by two distinct paths without considering the intermediate formation of the carbene. Alternatively, the diazirine may decompose to yield only t-butylcarbene and nitrogen, if one postulates that the carbene is formed with two distinct energy levels (possibly different electronic states). The mechanism would then be:



Such a mechanism would have the same kinetic consequences as the one already suggested, and the data here presented do not allow a choice between them. In support of this mechanism, we note that the results obtained in the mercury-sensitised decomposition of ethylene may be explained in terms of a mechanism involving two excited states of ethylidene.[12] Methyl migration in the carbene to yield 2-methylbut-2-ene (reaction 12) is a reaction already noted in other carbenes.[13]

We return now to the curvature which is observed if the plot shown in Figure 4 is extended to cover the complete pressure range studied. This curvature is of a type noticed previously in other work with diazirines, and also in the isomerisation of excited molecules produced by methylene addition reactions. It has been ascribed to " energy

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[9] H. M. Frey, *J.*, 1962, 2293.
[10] D. P. Chong and G. B. Kistiakowsky, *J. Phys. Chem.*, 1964, **68**, 1793.
[11] W. Kirmse, " Carbene Chemistry," Academic Press, London, 1964.
[12] D. W. Setser, B. S. Rabinovitch, and D. W. Placzek, *J. Amer. Chem. Soc.*, 1963, **85**, 862.
[13] H. Philip and J. Keating, *Tetrahedron Letters*, 1961, 523.

spread" in the vibrationally excited molecules of the cyclopropanes. All the more-recently-developed theories of unimolecular reactions predict that the lifetimes of molecules undergoing such transformations will be energy-dependent, and this prediction has been amply verified experimentally. This implies, in the present case, that $k_6$, $k_7$, and $k_8$ will vary with the energy content of the excited 1,1-dimethylcyclopropane. Thus the observed curvature can be easily accounted for if it is assumed that the molecules of the cyclopropane have a relatively small " energy spread."

It might be argued that it is unnecessary to postulate two distinct paths for the formation of the 1,1-dimethylcyclopropane. Rather, that a reaction produces the cyclopropane molecules with a wide range of energies, of which some 25% contain insufficient energy to decompose. It is easy to show that such a mechanism would not account for the observed results. Excited molecules produced in this fashion would have an enormous range of lifetimes, and not only would there be no linear part of Figure 4, but also the curvature would be enormously greater. (A comparison of these results with those obtained in the " fall-off " region for the rate constants obtained in the thermal isomerisation of 1,1-dimethylcyclopropane, where the energy spread is far less than would be required by this mechanism, makes this quite clear.)

If the excited molecules of 1,1-dimethylcyclopropane are stabilised on every collision (reaction 5), then we can calculate the average lifetime of the cyclopropane molecules. From the slope of the plot shown in Figure 4, in the linear region, this is *ca.* $3{\cdot}7 \times 10^{-9}$ sec. (We have taken the collision frequency to be $9{\cdot}9 \times 10^{9}$ sec.$^{-1}$ at 760 mm. and 60°.) The reciprocal of this value, $2{\cdot}7 \times 10^{8}$ sec.$^{-1}$, is equal to $(k_6 + k_7 + k_8)$. Setser and Rabinovitch [14] have calculated that, in the case of 1,1-dimethylcyclopropane produced by the addition of methylene to isobutene, where the sum of the rate constants for isomerisation is $1{\cdot}9 \times 10^{8}$ sec.$^{-1}$, the average energy content of the excited molecule is 119 kcal./mole. With the present value of $2{\cdot}7 \times 10^{8}$ sec.$^{-1}$, the average energy content must be about 121 kcal./mole. Since the energy of the photolytic radiation is about 90 kcal./mole, this implies that $\Delta H_f$(t-butyldiazirine) $-$ $\Delta H_f$(1,1-dimethylcyclopropane) must be greater than 30 kcal./mole (in fact, considerably greater, if the nitrogen carries off an appreciable fraction of the energy of the system). This is certainly quite probable, especially as it has already been shown that diazirine itself is 30 kcal./mole more endothermic than the already highly endothermic diazomethane.[15]

In the thermal isomerisation of 1,1-dimethylcyclopropane,[16] the major products are 2-methylbut-2-ene and 3-methylbut-1-ene, formed in roughly equal amounts, together with much smaller quantities of 2-methylbut-1-ene. At the temperatures of the experiments, the 3-methylbut-1-ene itself was found to undergo slow decomposition to yield the other two olefins. It was not possible to say with certainty whether any of the 2-methylbut-1-ene arose from the 1,1-dimethylcyclopropane directly, or whether it was all formed by the secondary reactions.

In the present work, the formation of the three olefins is qualitatively in agreement with the thermal experiments. However, the suggested mechanism requires that the ratios of the olefins formed by isomerisation from the dimethylcyclopropane should remain constant throughout the pressure range. A small effect due to the different variations of $k_6$, $k_7$, and $k_8$ with energy content is to be expected, but this would almost certainly be less than the experimental errors in the present system. In fact, the ratios $k_6 : k_7 : k_8$ show large variations over the pressure range studied. At high pressures, where there is little isomerisation (and no detectable amount of 2-methylbut-1-ene), the ratio $k_6 : k_7$ is constant and close to unity. However, at lower pressures, the yield of 2-methylbut-2-ene increases much more rapidly than that of 3-methylbut-1-ene. Since the molecules of these olefins, when initially formed from the 1,1-dimethylcyclopropane, must themselves

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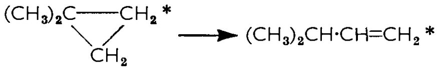
[14] D. W. Setser and B. S. Rabinovitch, *Canad. J. Chem.*, 1961, **40**, 1425.

[15] G. S. Paulett and R. Ettinger, *J. Chem. Phys.*, 1963, **39**, 825.

[16] M. C. Flowers and H. M. Frey, *J.*, 1959, 3953; 1962, 1157.

be highly vibrationally excited, it is probable that they require collisional deactivation to become stabilised. Thus reaction (7) should more correctly be written:

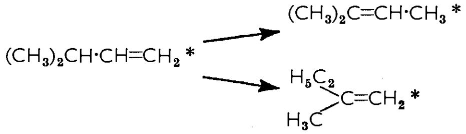


(7*a*)

followed by

$$(CH_3)_2CH{\cdot}CH{=}CH_2{}^* + M \longrightarrow (CH_3)_2CH{\cdot}CH{=}CH_2 \qquad (15)$$

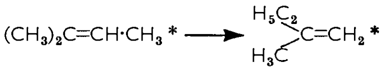
[There will be a similar reaction (6*a*) instead of (6).] This opens up the possibility of reactions such as:



$$(CH_3)_2CH{\cdot}CH{=}CH_2{}^* \longrightarrow (CH_3)_2C{=}CH{\cdot}CH_3{}^* \qquad (16)$$

$$(CH_3)_2CH{\cdot}CH{=}CH_2{}^* \longrightarrow (H_5C_2)(H_3C)C{=}CH_2{}^* \qquad (17)$$

and also



$$(CH_3)_2C{=}CH{\cdot}CH_3{}^* \longrightarrow (H_5C_2)(H_3C)C{=}CH_2{}^* \qquad (18)$$

These reactions have previously been suggested in high-energy systems[14] and would account quite simply for the observed variation in yields of the olefins. In particular, they would account for the very rapid increase in the yield of 2-methylbut-1-ene at the lowest pressure. An additional feature in support of this modified mechanism is shown by the yields of 2-methylbut-2-ene at the lowest pressure, where they apparently go through a maximum. While the experimental data are not sufficiently precise for the location of the exact position of the maximum in Figure 2, there is no doubt of its existence, since several repeat experiments, at the lowest pressure, gave values for the yield of 2-methylbut-2-ene which were less than those obtained at somewhat higher pressures. This would be due to reactions of type (18) becoming of greater importance at these pressures. This is to be expected, and, further, since 2-methylbut-2-ene is thermodynamically the most stable of the three olefins, this reaction will be significant at pressures lower than those at which reactions (16) and (17) start to become important. It should be noted that, provided the excited olefins only undergo isomerisation reactions of the type suggested, equation (9) will still be valid. Finally, with the modified mechanism, it is no longer certain how much (if any) of the observed 2-methylbut-1-ene arises directly from the 1,1-dimethylcyclopropane.

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