Kinetics of Methylene Addition to *cis*- and *trans*-But-2-ene

Further Evidence for the Energy Separation between Triplet and Singlet Methylene

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The reactions of triplet and singlet methylene with *cis*- and *trans*-but-2-ene have been studied over the temperature range 350-473 K. The results yield a value of (36.5 ± 3.2) kJ mol^{-1} for the energy separation between singlet and triplet methylene, and provide further confirmation of the assumption that singlet methylene reactions with hydrocarbons proceed with activation energies close to zero. Previous evidence for the similar reactivities of triplet methylene and the methyl radical receives additional support.

Recent theoretical calculations [1] of the energy separation between the triplet ($^3B_1$) and the singlet ($^1A_1$) states of methylene lead to a value of (46 ± 8) kJ mol^{-1}. A reinterpretation of earlier experimental data [2] yielded a lower limit of 34 kJ mol^{-1} for this separation, in sharp contrast to the much smaller values of 4-10 kJ mol^{-1} derived earlier.[3] In a preliminary report of this work [4] a value of 38 kJ mol^{-1} was obtained. The additional studies reported here provide further confirmation of this value.

EXPERIMENTAL

MATERIALS

Keten was prepared by the pyrolysis of acetic anhydride [5] and purified by several trap-to-trap distillations from −130 to −160°C. It was stored as a gas at pressures below 100 Torr in blackened glass vessels. It was degassed before each run at −196°C.

Nitrogen (B.O.C. oxygen free grade) was used without purification.

Cis-but-2-ene and *trans*-but-2-ene (Matheson Instrument Grade) were better than 99 % pure and were used without further purification.

APPARATUS

A conventional high vacuum line was used for all gas handling. Teflon–glass stopcocks were used throughout to minimise absorption problems.

All photolyses were carried out in a Pyrex reaction cell using the unfiltered output of an Osram HBO 200 W super pressure mercury lamp. The cell was thermostatted in an aluminium furnace. Temperature variations over the cell surface were less than ± 1°C from the mean temperature of the cell. Temperature measurements were made using chromel-alumel thermocouples.

ANALYSIS

All quantitative analyses were by gas chromatography, using a Perkin Elmer 452 gas chromatograph with a flame ionisation detector. A 100 m PPG capillary column at 0°C was used. The retention times of all the products of interest were determined from pure samples. The detector response to the products, all C_5 hydrocarbons, was assumed to be equal. The product ratios were determined by peak height measurements, corrected for retention times.

PROCEDURE

Photolysis mixtures consisted of keten, *cis*- or *trans*-but-2-ene and nitrogen in the ratio 1 : 2 : 30. Total pressures were in the range 600-700 Torr. A few experiments were carried out using a ratio 1 : 2 : 200. The mixtures were photolysed and the non-condensable gases removed at −196°C. Most runs yielded sufficient products for two analyses; for all runs reported, the product ratios for duplicate analyses were reproducible to better than ±5 %. The product ratios were reproducible to ±10 % from separate runs under identical conditions.

RESULTS

The following reaction scheme represents the important processes occurring:

$$CH_2CO \xrightarrow{h\nu} CH_2 + CO \tag{1}$$

$$^3CH_2 + M \rightleftharpoons {}^1CH_2 + M \tag{2}$$

$$^3CH_2 + \underset{(CB2)}{cis\text{-but-2-ene}} \rightarrow \underset{(DMCP)}{cis\text{-} + trans\text{-dimethyl cyclopropane}} \tag{3a}$$

$$^1CH_2 + CB2 \rightarrow cis\text{-DMCP} \tag{4a}$$

$$^1CH_2 + CB2 \rightarrow \text{2-methylbut-2-ene (2MB2)} \tag{5a}$$

$$^1CH_2 + CB2 \rightarrow cis\text{-pent-2-ene (CP2)} \tag{6a}$$

$$^3CH_2 + CB2 \rightarrow CH_3\cdot + (\text{butenyl})\cdot \tag{7a}$$

$$^3CH_2 + trans\text{-but-2-ene (TB2)} \rightarrow cis\text{-} + trans\text{-DMCP} \tag{3b}$$

$$^1CH_2 + TB2 \rightarrow trans\text{-DMCP} \tag{4b}$$

$$^1CH_2 + TB2 \rightarrow 2MB2 \tag{5b}$$

$$^1CH_2 + TB2 \rightarrow trans\text{-pent-2-ene (TP2)} \tag{6b}$$

$$^3CH_2 + TB2 \rightarrow CH_3\cdot + (\text{butenyl})\cdot \tag{7b}$$

$$CH_3\cdot + (\text{butenyl})\cdot \rightarrow \text{3-methylbut-1-ene (3MB1)} \tag{8}$$

$$CH_3\cdot + (\text{butenyl})\cdot \rightarrow CP2 \tag{9}$$

$$CH_3\cdot + (\text{butenyl})\cdot \rightarrow TP2 \tag{10}$$

$$CH_3\cdot + CH_3\cdot \rightarrow \text{ethane} \tag{11}$$

$$2(\text{butenyl})\cdot \rightarrow C_8 \text{ hydrocarbons.} \tag{12}$$

On the assumption, discussed below, that reactions (2) and (−2) maintain an equilibrium ratio of singlet to triplet methylene in the presence of a thirty-fold excess of inert gas the following relations may be derived:

$$\log[(cis\text{-DMCP}/trans\text{-DMCP}) - 0.30] = \log(0.43A_{4a}/A_{3a}) - (\Delta E_2 - E_{3a})/2.303\,RT \tag{1}$$

and

$$\log[(trans\text{-DMCP}/cis\text{-DMCP}) - 3.40] = \log(1.45A_{4b}/A_{3b}) - (\Delta E_2 - E_{3b})/2.303\,RT \tag{2}$$

where ΔE_2 is the energy separation between the two spin states of methylene, E_{3a} and E_{3b} are the energies of activation of reactions (3*a*) and (3*b*) respectively and A_{3a}, A_{3b}, A_{4a} and A_{4b} are the Arrhenius pre-exponential factors for reactions (3*a*), (3*b*), (4*a*) and (4*b*) respectively. In the derivation of relations (1) and (2) the same value for the ratio (*trans*-DMCP/*cis*-DMCP) has been assumed in reactions (3*a*) and (3*b*). The value (3.40) for this isomer ratio has been taken from Montague's study of the mercury photosensitised isomerisation of 3-methylbut-1-ene.[6] Thus the l.h.s. in eqn (1) and (2) are corrected for the fraction of stereospecific product arising from the triplet reactions (3*a*) and (3*b*) respectively. It has also been assumed that the singlet addition reactions (4*a*) and (4*b*) proceed with zero activation energies. Plots of the left hand sides of eqn (1) and (2) against $1/T$ are shown in fig. 1.

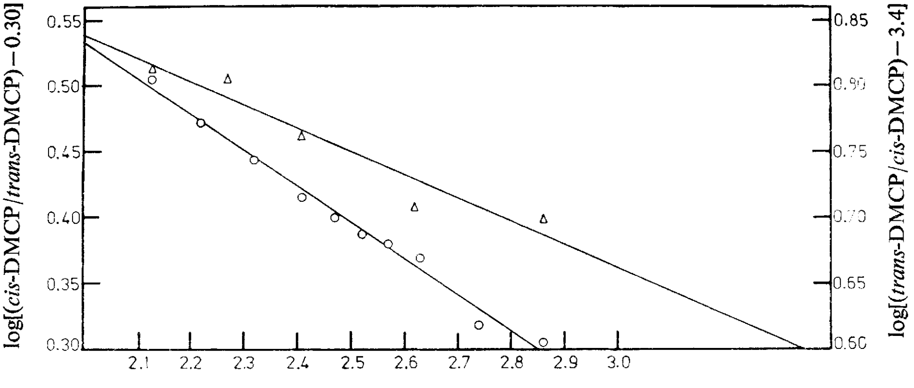

FIG. 1.—Ratio of geometric isomers of 1,2-dimethyl-cyclopropane as a function of temperature. ○, Using CB2 (l.h. axis): △, using TB2 (r.h. axis).

Accepting the value of 1.39 for the ratios(TP2/CP2)[7] produced by reactions (9) and (10) the contribution from triplet reaction to the product CP2 in the CB2 system and to the product TP2 in the TB2 system may be separated from the singlet contribution to these products arising from reactions (6*a*) and (6*b*): the two contributions to these products will be designated s- and t-CP2 and TP2. The triplet contribution to *cis*-DMCP (CB2 system) and to *trans*-DMCP (TB2 system) may be separated from the yields of these products arising from the singlet reactions (4*a*) and (4*b*): the two contributions to the total yield of these products may be similarly distinguished. According to the reaction scheme above 2MB2 arises only from the singlet reactions (5*a*) and (5*b*). The following relations may then be derived for the CB2 system:

$$\log(\text{s-CP2/s-}cis\text{-DMCP}) = \log(A_{6a}/A_{4a}) - (E_{6a} - E_{4a})/2.303\,RT \tag{3}$$

$$\log(\text{2MB2/s-}cis\text{-DMCP}) = \log(A_{5a}/A_{4a}) - (E_{5a} - E_{4a})/2.303\,RT. \tag{4}$$

Analogous relations may be derived for the TB2 system.

Representative data for the temperature dependence of the ratios 2MB2/s-*cis*-DMCP and s-CP2/s-*cis*-DMCP, (CB2 system) and 2MB2/s-*trans*-DMCP and s-TP2/s-*trans*-DMCP, (TB2 system) are shown in table 1. The data indicate no systematic variation of these product ratios with temperature.

TABLE 1.—PRODUCT RATIOS AS A FUNCTION OF TEMPERATURE

10^3 K/T	2MB2/s-*cis*-DMCP	s-CP2/s-*cis*-DMCP	2MB2/s-*trans*-DMCP	s-TP2/s-*trans*-DMCP
2.30	0.38	0.74	0.27	0.88
2.41	0.33	0.70	0.20	0.84
2.47	0.34	0.78		
2.52	0.30	0.71		
2.57	0.32	0.72		
2.63	0.31	0.70	0.23	0.83
2.74	0.31	0.69		
2.86	0.30		0.18	0.82

Adding t-*cis*-DMCP to the measured *trans*-DMCP in the CB2 system gives the total yield of reaction (3*a*); the yield of reaction (3*b*) in the TB2 system may be similarly determined. If is is assumed that the activation energies of the radical–radical reactions (8)-(12) are close to zero the following relation may be derived for the CB2 system:

$$\log 3\text{MB1}/(\text{t-}cis\text{-DMCP}+trans\text{-DMCP}) = \log(A_{7a}/A_{3a})-(E_{7a}-E_{3a})/2.303\,RT. \quad (5)$$

An analogous relation may be derived for the TB2 system. Plots of the left hand sides of these equations are shown in fig. 2.

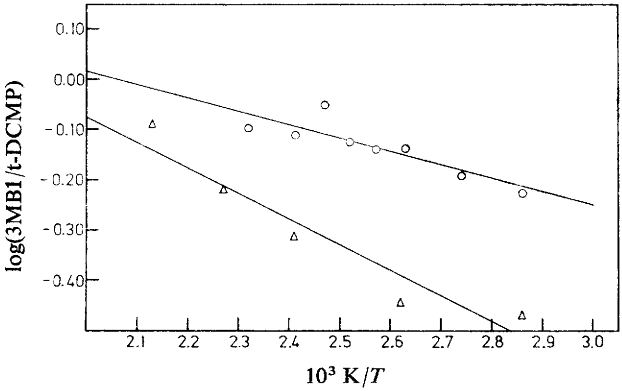

FIG. 2.—Ratio of 3-methylbut-1-ene to t-1,2-dimethylcyclopropane as a function of temperature. ○, Using CB2: △, using TB2.

In order to evaluate ΔE_2 from the values of (ΔE_2-E_{3a}) and (ΔE_2-E_{3b}) given by eqn (1) and (2) we have previously assumed [4] that E_{3_a} and E_{3_b} are equal to the experimentally determined activation energies [8] for methyl radical addition to CB2 and TB2 respectively. If the additional assumption is made that A_{3_a} and A_{3_b} are equal to the A factors for methyl radical addition to the two olefins the evaluation of the ratios (A_{4a}/A_{3a}) and (A_{4b}/A_{3b}) on the basis of eqn (1) and (2) permits an evaluation of A_{4_a} and A_{4_b} as a fraction of the collisional rate.

The values of the parameters derived from the above analysis are summarised in table 2.

TABLE 2.—ACTIVATION ENERGY DIFFERENCES AND A-FACTOR RATIOS

A-factor ratios	activation energy differences/kJ mol^{-1}
	$\Delta E_2-E_{3a} = 5.3\pm0.2$ [a, b]
	$\Delta E_2-E_{3b} = 3.4\pm0.5$ [a, b]
$A_{4a}/A_{3a} = 28.2\pm1.7$ [c]	
$A_{4b}/A_{3b} = 10.8\pm2.0$ [c]	
$A_{5a}/A_{4a} = 0.33\pm0.5$	$E_{5a}-E_{4a} \approx 0$
$A_{5b}/A_{4b} = 0.22\pm0.03$	$E_{5b}-E_{4b} \approx 0$
$A_{6a}/A_{4a} = 0.72\pm0.05$	$E_{6a}-E_{4a} \approx 0$
$A_{6b}/A_{4b} = 0.86\pm0.05$	$E_{6b}-E_{4b} \approx 0$
$A_{1a}/A_{3a} = 3.5\pm1.5$	$E_{1a}-E_{3a} = 5.0\pm1.3$
$A_{1b}/A_{3b} = 9.3\pm3.7$	$E_{1b}-E_{3b} = 10.0\pm1.7$

[a] ΔE_2 is the energy separation between the two spin states; [b] if E_{3a} and E_{3b} are assumed to be (30.6 ± 2.0) kJ mol^{-1} and (33.8 ± 2.0) kJ mol^{-1} respectively, then values of (35.9 ± 2.1) kJ mol^{-1} and (37.2 ± 2.5) kJ mol^{-1} for ΔE_2 result. The mean value of ΔE_2 from the two systems is thus (36.5 ± 3.2) kJ mol^{-1} (see text); [c] if values of $10^{7.65}$ dm^3 mol^{-1} s^{-1} and $10^{8.15}$ dm^3 mol^{-1} s^{-1} are assumed for A_{3a} and A_{3b} respectively, values of 5.6×10^{-3} and 6.8×10^{-3} for the ratios of A_{4a} and A_{4b} respectively to the collisional rate result.

DISCUSSION

It is well known[9] that the photolysis of keten (1) at wavelengths shorter than 366 nm produces methylene in both triplet and singlet states, the latter spin state increasingly predominating at shorter wavelengths. We assume, on the basis of Carr's work,[10] that in the presence of a thirtyfold excess of nitrogen the non-equilibrium ratio of the spin states produced by (1) is brought to equilibrium by the inter-system crossing reaction (2) and (−2) and, thus, that the subsequent reactions (3)-(12) involve equilibrium populations of the two spin states. Runs carried out in the presence of a hundred-fold excess of nitrogen gave product distributions identical to those reported using a thirtyfold excess, confirming this assumption.

Though the products of reactions (3*a*)-(6*a*) and (3*b*)-(6*b*) are chemically activated upon formation, there is ample evidence from other work[11] that the half-pressures for stabilisation of the hot molecules are 70 Torr or less. Thus at the pressures used in this work (600-700 Torr), chemically activated decompositions and isomerisations of the products of reactions (3*a*)-(6*a*) and (3*b*)-(6*b*) will not occur to a significant extent.

Montague[6] has shown that the isomer ratio (*trans*-DMCP/*cis*-DMCP) arising from the ring closure of the biradical initially formed in reactions (3*a*) and (3*b*) is pressure-dependent. If it is assumed that the triplet biradical is in conformational equilibrium at each energy level during collisional deactivation, then the pressure dependence of the isomer ratio will reflect the pressure dependence of the mean energy level from which the final deactivating collision occurs. On the basis of this interpretation the initial excess energy of the biradical is unimportant and the temperature dependence of the ratio is unlikely to be strong. We have thus used the value 3.4 for the product ratio (*trans*-DMCP/*cis*-DMCP) arising from reactions (3*a*) and (3*b*), as determined by Montague for the pressure range of this study.

Since it is known that the activation energies for hydrogen abstraction from *cis*- and *trans*-but-2-ene by methyl radicals are similar to the activation energies for addition, on the basis of the similar reactivities of triplet methylene and the methyl radical discussed below, reactions (7*a*) and (7*b*) are expected to occur at rates comparable to those of reactions (3*a*) and (3*b*) respectively. The presence of ethane in the product mixture is evidence for methyl radical participation and, as noted above, it is unlikely to be produced in significant amounts by decomposition of the biradical intermediate of reactions (3*a*) and (3*b*) in the pressure range of this study. The addition of 10 % of oxygen to the reactant mixture suppresses completely the production of ethane and 3MB1 in both the CB2 and the TB2 systems, TP2 in the CB2 system and CP2 in the TB2 system. Since oxygen is known to suppress the reactions of triplet methylene very efficiently this further confirms that the above scheme represents all the significant reactions occurring in the two systems.

We thus derive values of (36±2) and (37±2) kJ mol^{-1} from the CB2 and TB2 systems respectively for the energy separation between singlet and triplet methylene. These values are in good agreement both with the results of recent theoretical calculations and with the experimental results of Hase *et al.*,[12] Simons and Curry[13] and Lahmani.[14] The key difference between our interpretation of these systems and the earlier interpretations which led to very much lower values for the energy separation is our assumption that collisional reactivation of the triplet to the singlet, reaction (2), is significant. Thus, in the presence of a sufficient excess of inert gas, the reactions of an equilibrium population ratio of the two spin states can be studied. That earlier work[15] reveals the presence of insertion products in the presence of an excess of inert gas sufficient[10, 16] to deactivate the singlet quantitatively to the triplet is evidence for the occurrence of reaction (2). That a substantial change in the inert gas/substrate ratio produces no change in the product ratios, as reported above, is evidence that an equilibrium ratio of the two spin states is being studied.

The major assumption made in the derivation of the above values is the use of Arrhenius parameters for triplet methylene derived from analogous reactions of the methyl radical. The evidence for the validity of this assumption is less direct. However, on the basis of this assumption we have derived values of the ratios A_{4a}/collision rate and A_{4b}/collision rate which are in good agreement with the value of 5×10^{-3} derived from flash photolysis studies [16] for the insertion of singlet methylene into methane. The values derived for the activation energy difference $(E_{3b}-E_{3a})$ *viz.*, (2.0 ± 0.7) kJ mol^{-1}, for addition to the two olefins and for the differences $(E_{7a}-E_{3a})$ and $(E_{7b}-E_{3b})$ *viz.*, 5 and 10 kJ mol^{-1} respectively are of comparable magnitude to the relative activation energies determined [8] for the analogous methyl radical reactions. The magnitudes of these assumed activation energies for the triplet are also in general agreement with the results of Carr's BEBO calculations.[17] Finally, Lahmani's result of (31.4 ± 3.0) kJ mol^{-1} for the energy separation is derived from an experimentally determined rate ratio of $(5 \pm 2 \times 10^4)$ for the following reactions

$$^1CH_2 + C_3H_8 \rightarrow C_4H_{10}$$

$$^3CH_2 + C_3H_8 \rightarrow CH_3{\cdot}C_3H_7{\cdot}.$$

Precise agreement with our derived value for the energy separation would require a value of 1.9×10^5 for this rate ratio. Rowland *et al.*[18] derive a value $> 10^7$ for this ratio, which is close to the value derived using the experimental Arrhenius parameters for the analogous reaction of the methyl radical with propane.[19] A value of 10^7 in Lahmani's calculation yields a value for the energy separation of 44.5 kJ mol^{-1}. Thus, pending a direct determination of the Arrhenius parameters for the triplet reaction, our present assumption is vindicated by its consistency with the results of these other studies.

We have derived values for the relative rates of the three possible singlet reactions with the two olefins. Our results indicate no temperature dependence of these relative rates within the limits of the experimental accuracy. Further, the ratio of vinylic to methyl C—H bond insertion is close to 0.33 in both olefins, as anticipated if insertion proceeds with equal probability in all C—H bonds. Taken in conjunction with the agreement of the singlet addition rates with the absolute value of Braun, Bass and Pilling [17] for methane, these results support the commonly held assumption that singlet methylene reactions with hydrocarbons proceed with activation energies close to zero.

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