Kinetics of Decomposition and Interconversion of 3-Methylbut-1-yne and 3-Methylbuta-1,2-diene. Resonance Stabilization Energies of Propargylic Radicals
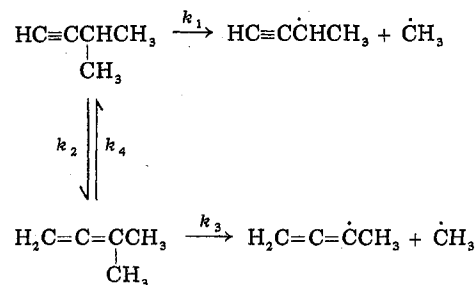
Tam T. Nguyen and Keith D. King*

Department of Chemical Engineering, University of Adelaide, Adelaide, South Australia 5001 (Received: March 24, 1981; In Final Form: June 24, 1981)

The thermal unimolecular reactions of 3-methylbut-1-yne (MBT) and 3-methylbuta-1,2-diene (MBTD) have been studied over the temperature range 940–1222 K by using the technique of very low-pressure pyrolysis (VLPP). Both compounds decompose via C_3–C_4 bond fission producing the resonance-stabilized radicals, 1-methylpropargyl from MBT and 1-methylallenyl from MBTD. In addition, interconversion between the two reactants takes place via structural isomerization. RRKM calculations, incorporating competing pathways and a temperature-dependent gas/wall collision efficiency, show that the experimental rate constants are consistent with the following high-pressure specific rate expressions at 1100 K: $\log (k_1/s^{-1}) = (16.3 \pm 0.3) - (71.6 \pm 1.0)/\theta$ for bond fission and $\log (k_2/s^{-1}) = (13.2 \pm 0.6) - (60.5 \pm 1.0)/\theta$ for isomerization for MBT, $\log (k_3/s^{-1}) = (16.3 \pm 0.3) - (75.3 \pm 1.0)/\theta$ for bond fission and $\log (k_4/s^{-1}) = (13.2 \pm 0.6) - (63.8 \pm 1.0)/\theta$ for isomerization for MBTD, where $\theta = 2.303RT$ kcal/mol. The A factor for bond fission was assigned from the results of recent shock-tube studies of related alkynes, and the A factor for isomerization was adopted from that previously reported for the analogous allene $\rightleftharpoons$ propyne interconversion. The results lead to $\Delta H_f^\circ{}_{300}[HCC\dot{C}HCH_3] = 72.4$, $DH^\circ{}_{300}[HCCCH(CH_3)-H] = 85.0$, $\Delta H_f^\circ{}_{300}[H_2CC\dot{C}CH_3] = 74.3$, and $DH^\circ{}_{300}[CH_3CC\dot{C}H_2-H] = 91.4$ kcal/mol. The resonance stabilization energies are 10.0 ± 2.2 and 7.8 ± 2.2 kcal/mol for the 1-methylpropargyl and 1-methylallenyl radicals, respectively, in reasonable agreement with previous results for other propargylic radicals. The activation energy for the isomerization MBTD $\rightarrow$ MBT is similar to that previously reported for the conversion of allene to propyne, and the equilibrium constants for the interconversion MBT $\rightleftharpoons$ MBTD calculated from the rate data show good agreement with the values estimated from thermodynamic data over the experimental temperature range.

Introduction

The heat of formation and resonance stabilization energy of the propargyl radical have now been well established to be 81.5 ± 1.0 and 8.7 ± 1.0 kcal/mol from the combined results of very low-pressure pyrolysis (VLPP)[1-3] and shock-tube[4,5] studies. Methyl substituents on both the radical site and the terminal carbon atom have been found to have little effect on the propargyl resonance energy.[2,5-7]

In the present VLPP study kinetic data are reported for the thermal decomposition of 3-methylbut-1-yne (MBT) and 3-methylbuta-1,2-diene (MBTD). MBT was chosen with an aim to complete the series of butynes (but-1-yne[1] and 3,3-dimethylbut-1-yne[2] have already been studied) and thus provide thermochemical data pertaining to the 1-methylpropargyl radical, $HC\equiv C\dot{C}H(CH_3)$. A complication was the isomerization of MBT to MBTD (and its reverse) under the experimental conditions. Although similar processes have not been observed in previous VLPP and shock-tube experiments using long-chain alkynes ($\geq C_4$), shock-tube studies of isomerization in the analogous system, allene $\rightleftharpoons$ propyne, have been previously reported.[8-10] MBTD should also undergo C_3–C_4 bond fission to produce 1-methylallenyl, $H_2C\equiv C\equiv \dot{C}CH_3$ and methyl radicals. The reaction schemes for MBT and MBTD can be represented as follows:

(1) King, K. D. *Int. J. Chem. Kinet.* **1978**, *10*, 545.
(2) King, K. D. *Int. J. Chem. Kinet.* **1977**, *9*, 907.
(3) King, K. D.; Nguyen, T. T. *J. Phys. Chem.* **1979**, *83*, 1940.
(4) Tsang, W. *Int. J. Chem. Kinet.* **1970**, *2*, 23.
(5) Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 687.
(6) Martin, M. M.; Sanders, E. B. *J. Am. Chem. Soc.* **1967**, *89*, 3777.
(7) King, K. D.; Nguyen, T. T. *Int. Chem. Kinet.* **1981**, *13*, 255.
(8) Lifshitz, A.; Frenklach, M.; Burcat, A. *J. Phys. Chem.* **1975**, *79*, 1148.
(9) Bradley, J. N.; West, K. O. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1337.
(10) Simmie, J. M.; Melvin, D. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1337.

$$HC\equiv CCHCH_3 \xrightarrow{k_1} HC\equiv C\dot{C}HCH_3 + \dot{C}H_3$$
$$\underset{CH_3}{|}$$

$$k_2 \big\Updownarrow k_4$$

$$H_2C\equiv C\equiv CCH_3 \xrightarrow{k_3} H_2C\equiv C\equiv \dot{C}CH_3 + \dot{C}H_3$$
$$\underset{CH_3}{|}$$

Note that 1-methylpropargyl and 1-methylallenyl are not the same radical. The former is a resonance hybrid (or mesomeric structure) of the two valence bond forms

$$HC\equiv C\dot{C}H(CH_3) \leftrightarrow H\dot{C}\equiv C\equiv CH(CH_3)$$
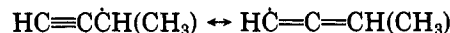
while the latter is a resonance hybrid of the forms

$$H_2C\equiv C\equiv \dot{C}CH_3 \leftrightarrow H_2\dot{C}C\equiv CCH_3$$
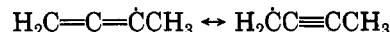
We have also obtained kinetic data on the formation of the 1-methylallenyl (or 3-methylpropargyl) radical from pyrolysis of pent-2-yne.[11]

Experimental Section

MBT (K & K) and MBTD (Columbia Organic Chemicals) were thoroughly degassed and vacuum distilled bulb-to-bulb before use. The VLPP experimental system and technique have been described in detail;[12] reactor II was employed.[3] It has three interchangeable exit apertures with reactor collision numbers, Z, of 21 460, 2177, and 260. The gas/wall collision frequency, $\omega = (4.09 \times 10^3)(T/M)^{1/2}$ s^{-1}, where T is temperature in Kelvin and M is mass in amu.

(11) King, K. D.; Nguyen, T. T., manuscript in preparation.
(12) King, K. D.; Goddard, R. D. *Int. J. Chem. Kinet.* **1975**, *7*, 109.

Results

MBT. The mass spectrum of undecomposed MBT at 9-eV ionizer electron energy showed a most intense peak at m/e 67 and weaker peaks at m/e 68 (molecular), 53, 42, 40, 15, and 12. At 1072 K the reaction mixture representing ca. 70% total disappearance of MBT (1-mm aperture, $Z = 21460$) had a major peak at m/e 68 and other less intense ones at m/e 67, 66, 54, 53, 52, 42, 40, 39, 28, 15, and 12. The peak at m/e 53 is attributable to the 1-methylpropargyl radical. The decrease of the peak at m/e 67 together with the substantial increase of the peak at m/e 15 due to methyl radicals confirm that reaction 1 is a primary process in the pyrolysis of MBT. The propargylic radicals may decompose by ejecting H atoms according to reaction 5 to yield but-1-ene-3-yne while a

$$HC{\equiv}C\dot{C}HCH_3 \rightarrow HC{\equiv}CCH{=}CH_2 + H \qquad (5)$$

proportion of them may also react with a H-atom source (inside or outside the reactor) to form but-1-yne/buta-1,2-diene as found previously in similar reaction systems.[13] The observation of significant increases at m/e 52 and 54 is consistent with the existence of these molecular products. The considerable growth of the peak at m/e 68 can be related to the formation of MBTD from the isomerization of MBT (reaction 2). This molecular peak is the most intense in the mass spectrum of the former compound. After its formation MBTD is expected to undergo subsequent thermal decay via reaction 3. This was confirmed by the observation that the peak at m/e 68 started to grow at ~940 K ($Z = 21460$) and then began to diminish at ~1050 K.

MBT total disappearance was quantitatively monitored by the peak at m/e 67 with CF_4 (m/e 69) as an internal standard. These measurements were made by using 70-eV ionizing voltage and with the employment of two escape apertures ($Z = 21460$ and 2177) over the temperature range 941–1222 K.

MBTD. The mass spectrum of MBTD is quite similar to that of MBT except that the molecular peak at m/e 68 is the most intense. At ~70% total decomposition ($Z = 21460$), the mass spectrum of the reaction mixture showed that a decrease of the molecular peak was accompanied by increases at m/e 67, 54, 52, 28, 15, and 12. 1-Methylallenyl and methyl radicals were confirmed as the primary products of reaction 3. The former either decomposed to give butatriene (m/e 52) according to reaction 6 or reacted with a H-atom source inside or outside the

$$H_2C{=}C{=}\dot{C}CH_3 \rightarrow H_2C{=}C{=}C{=}CH_2 + H \qquad (6)$$
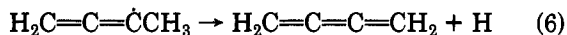
reactor to produce buta-1,2-diene/but-2-yne (m/e 54). The growth of the peak at m/e 67 at first increased (from ~970 K), and then began to decrease (from ~1100 K).
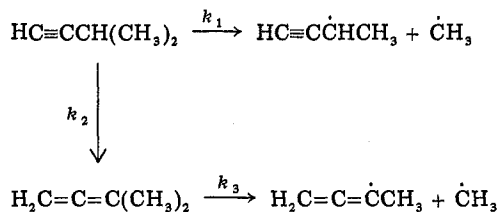
The total disappearance of MBTD was monitored by the peak at m/e 68 over the temperature range 971–1222 K with the use of the same two escape apertures as for MBT. CO_2 (m/e 44) and CF_4 (m/e 69) were used as internal standards in separate sets of experiments, the results from which were found to be in good agreement. Mass spectra were recorded at 70-eV ionizing voltage.

Determination of the Individual Rate Constants. Unimolecular rate constants for the total decay of MBT and MBTD were calculated in the usual way[14] from the expression $k_{uni} = k_e[f/(1 - f)]$, where k_e is the escape rate constant and f the fractional decomposition of the reactant

as calculated from mass-spectral peak intensities. The unimolecularity of the primary processes is confirmed by the nondependence of k_{uni} on the aperture size (and hence collision number, Z) and flow rates (1.6×10^{14}–12×10^{14} molecules/s for MBT, and 2.4×10^{14}–11×10^{14} molecules/s for MBTD).

For isomerization, starting from either compound experimental rate constants could be evaluated directly from product-formation data. However, this procedure was complicated by subsequent decay via C–C bond fission of the newly formed isomer above certain temperatures (see above). Direct measurement of the rate constants for either bond-fission pathway could not be obtained. However, by combining the VLPP data for separate experiments on both MBT and MBTD, one may obtain quantitive evaluation of the rate constants for individual pathways. The procedure is set out below.

For experiments with MBT as the reactant, the reactions involved can be summarized in the following scheme:

$$HC{\equiv}CCH(CH_3)_2 \xrightarrow{k_1} HC{\equiv}C\dot{C}HCH_3 + \dot{C}H_3$$

$$\downarrow k_2$$

$$H_2C{=}C{=}C(CH_3)_2 \xrightarrow{k_3} H_2C{=}C{=}\dot{C}CH_3 + \dot{C}H_3$$

The back isomerization of MBTD to MBT is assumed to be negligible (i.e., k_4 is disregarded) under these conditions.[15] The rate of the total decay of MBT is given by

$$-d[MBT]/dt = k_1[MBT] + k_2[MBT] \qquad (7)$$

and therefore

$$k_{obsd}(MBT) = k_1 + k_2 \qquad (8)$$

For VLPP conditions

$$k_e[MBTD] = k_2[MBT] - k_3[MBTD] \qquad (9)$$

therefore

$$\{[MBTD]/[MBT]\}_I \equiv k_2/(k_3 + k_e) \qquad (10)$$

In the case of MBTD as the initial reactant, there is isomerization from MBTD to MBT (with rate constant k_4), but again the back isomerization is assumed to be negligible (i.e., k_2 is now disregarded). The following relationships can then be obtained:

$$-d[MBTD]/dt = k_3[MBTD] + k_4[MBTD] \qquad (11)$$

$$k_{obsd}(MBTD) = k_3 + k_4 \qquad (12)$$

$$k_e[MBT] = k_4[MBTD] - k_1[MBT] \qquad (13)$$

$$\{[MBT]/[MBTD]\}_{II} = k_4/(k_1 + k_e) \qquad (14)$$

The product-to-reactant concentration ratios in eq 10 and 14 can be evaluated experimentally in each case from the ratio of mass-spectral peak intensities and calibration spectra of mixtures of product and reactant. The rate constants k_1, k_2, k_3, and k_4 thus can be obtained by solving 8, 10, 12, and 14:

$$k_1 = (k_e A_2 B_2 + A_1 - A_2 k_e - A_2 B_1)/(1 - A_2 B_2) \qquad (15)$$

$$k_2 = A_1 - k_1 \qquad (16)$$

$$k_3 = B_1 - k_4 \qquad (17)$$

$$k_4 = B_2(k_e + k_1) \qquad (18)$$

(13) Golden, D. M.; Piszkiewicz, L. W.; Perona, M. J.; Beadle, P. C. *J. Am. Chem. Soc.* 1974, *96*, 1645.

(14) Golden, D. M.; Spokes, G. N.; Benson, S. W. *Angew. Chem., Int. Ed. Engl.* 1973, *12*, 534.

(15) This assumption is supported by the fact that inclusion of the reverse isomerization in the kinetic scheme yielded negative values for some of the rate constants upon processing of the VLPP data.

TABLE I: Molecular Parameters in RRKM Calculations for MBT

	molecule	isomerization complex	bond-fission complex "vibration"	bond-fission complex "rotation"
frequencies (cm^{-1}) and degeneracies	3300 (1)	3030 (1)	3300 (1)	3300 (1)
	2950 (6)	2950 (6)	2950 (6)	2950 (6)
	2100 (1)	1860 (1)	2100 (1)	2100 (1)
	1460 (4)	1460 (4)	1460 (4)	1460 (4)
	1380 (2)	1380 (2)	1380 (2)	1380 (2)
	1300 (2)	1300 (2)	1300 (2)	1300 (2)
	1170 (2)	1160 (3)	1170 (2)	1170 (2)
	990 (5)	990 (6)	990 (3)	990 (3)
	630 (2)	700 (1)	625 (3)	630 (2)
	510 (1)	300 (1)	290 (1)	510 (1)
	340 (3)	200 (3)	270 (1)	240 (1)
	240 (1)	60 (1)	200 (1)	200 (1)
	200 (2)		90 (3)	
$10^{120}I_AI_BI_C{}^a/(\text{g cm}^2)^3$	0.6640×10^7	0.2138×10^7	0.4615×10^8	0.4615×10^8
$10^{40}I_r(\text{CH}_3 \cdots \text{CHC}(\text{CH}_3)\text{C}{\equiv}\text{CH})^{\ddagger}/(\text{g cm}^2)$			5.14	5.14
$10^{80}I_1I_2/(\text{g cm}^2)^2$				
methyl (two-dimensional)				$(3.18)^2$
propargyl (two-dimensional)				$(189.33)^2$
rpd^b		1	2	2
$I^{\ddagger}/I$			2.0	2.0
$S°_{300}/(\text{cal mol}^{-1}\text{ K}^{-1})$	76.3	76.7	87.9	92.8

^{a} One external rotation was chosen to be active in the bond-fission complexes (see text). ^{b} Reaction path degenerency.

where $A_1 \equiv k_{\text{obsd}}(\text{MBT})$, $A_2 \equiv \{[\text{MBTD}]/[\text{MBT}]\}_\text{I}$, $B_1 \equiv k_{\text{obsd}}(\text{MBTD})$, and $B_2 \equiv \{[\text{MBT}]/[\text{MBTD}]\}_\text{II}$. Least-squares polynomial fittings[16] were obtained for A_1, A_2, B_1, and B_2 over the experimental temperature ranges. The individual rate constants at any temperature could then be calculated by using appropriate values of the above parameters at that temperature and corresponding to the same escape aperture. The above procedure was confined to data representing overall conversions of ≤60% of initial reactant.

RRKM Calculations. The VLPP rate constants k_{uni} refer to the falloff regime and can be related to the high-pressure rate constants k_∞ by application of RRKM theory in the usual way.[17] This procedure in itself however does not produce an unambiguous set of Arrhenius parameters; a previous knowledge of either A_∞ or E_∞ is required. The postulation of an appropriate transition-state model is also necessary, but the exact details of the model are not important in determining the degree of falloff; the latter depends only on the Arrhenius parameters which the model is adjusted to fit.[17]

For simple bond fission in alkynes producing propargylic radicals, the commonly used vibrational model has been fully described previously.[18] This model has been shown to be satisfactory for those systems showing extensive electronic rearrangement in the incipient radicals.[19] The alternative, hindered rotational Gorin model,[20] on the other hand, has been shown to be capable of accommodating the negative temperature dependence of the A factors asso-

ciated with bond-fission processes.[21] The four low-frequency bending modes associated with the breaking bond are replaced by two two-dimensional hindered rotations of the fragments in the transition state. The merits of the hindered rotational model for alkyne systems have been examined in the VLPP studies of 4-methylpent-2-yne,[7] pent-1-yne,[22] and hex-1-yne.[23] Because of the successful application of the vibrational model to 4-phenylbut-1-yne,[3] but-1-yne,[1] and 3,3-dimethylbut-1-yne[2] (the latter two systems are closely related to the present study) and because of the known resonance stabilization of propargylic radicals, this model was adopted for MBT and MBTD. Nevertheless, for comparison, calculations were also performed by using a rotational transition-state model.

The A factors for alkyne bond fission have been shown by Tsang[4,5] to be fairly constant and lie within the range of $10^{16.0\pm0.3}$ s^{-1} per C–C bond broken. When this value is used in the analysis of VLPP data, the results for both VLPP and shock-tube studies are consistent.[23] When one takes into account reaction path degeneracies of 2 for both MBT and MBTD, an A factor of $10^{16.3}$ s^{-1} seems appropriate for these compounds.

Kinetic data on the isomerization of allene to propyne, $\text{CH}_2{=}\text{C}{=}\text{CH}_2 \rightleftharpoons \text{CH}_2\text{C}{\equiv}\text{CH}$, have been obtained in previous shock-tube studies.[8–10] Walsh[24] has shown that the results of Bradley and West[9] must be in error, but the Arrhenius parameters log $(A/\text{s}^{-1}) = 13.17$ and $E = 60.4$ kcal/mol obtained by Lifshitz et al.[8] seem to be reasonable. The limited results of Simmie and Melvin[10] are fairly consistent with the parameters of Liftshitz et al. Walsh[24] has further proposed that the conversion of allene to propyne may proceed in part via a pathway involving the intermediate formation of cyclopropene rather than entirely via a direct 1,3 hydrogen shift. This proposal is supported by recent studies of the interconversion of deuterium-labeled allene to propyne.[25] Using thermochemical kinetic arguments and recent data on the isomerization of cyclopropene to propyne, Walsh[26] has esti-

(16) Details of the polynomial expressions are as follows: $A_1 = 4.103 \times 10^3 - 16.144T + (23.873 \times 10^{-3})T^2 - (15.736 \times 10^{-6})T^3 + (3.9045 \times 10^{-9})T^4$; A_2(1-mm aperture) $= 1.2347 \times 10^3 - 4.6408T + (6.5079 \times 10^{-3})T^2 - (4.0376 \times 10^{-6})T^3 + (0.93615 \times 10^{-9})T^4$; A_2(3-mm aperture) $= -0.1329602564 \times 10^6 + (0.5938111751 \times 10^3)T - 1.059904229T^2 + (0.94511785 \times 10^{-3})T^3 - (0.421025 \times 10^{-6})T^4 + (0.7495948767 \times 10^{-10})T^5$; $B_1 = \exp\{2.303[-0.1798 \times 10^2 + 0.02491T - (0.78074 \times 10^{-5})T^2]\}$; B_2(1-mm aperture) $= 89.01 - 0.25253T + (0.23634 \times 10^{-3})T^2 - (72.756 \times 10^{-9})T^3$; B_2(3-mm aperture) $= (0.1811 \times 10^{-2})T - 1.949$.

(17) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley: London, 1972.

(18) Forst, W. "Theory of Unimolecular Reactions"; Academic Press: New York, 1973.

(19) Rossi, M.; King, K. D.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1223.

(20) Benson, S. W.; Golden, D. M. In "Physical Chemistry: An Advanced Treatise"; Eyring, H., Henderson, D., Jost, W., Eds.; Academic Press: New York, 1975; Volume 7. Smith, G. P.; Golden, D. M. *Int. J. Chem. Kinet.* **1978**, *10*, 489.

(21) Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 821.

(22) King, K. D. *Int. J. Chem. Kinet.* **1981**, *13*, 245.

(23) King, K. D. *Int. J. Chem. Kinet.* **1981**, *13*, 273.

(24) Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2137.

(25) Hopf, H.; Priebe, H.; Walsh, R. *J. Am. Chem. Soc.* **1980**, *102*, 1210.

(26) Bailey, I. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1146.

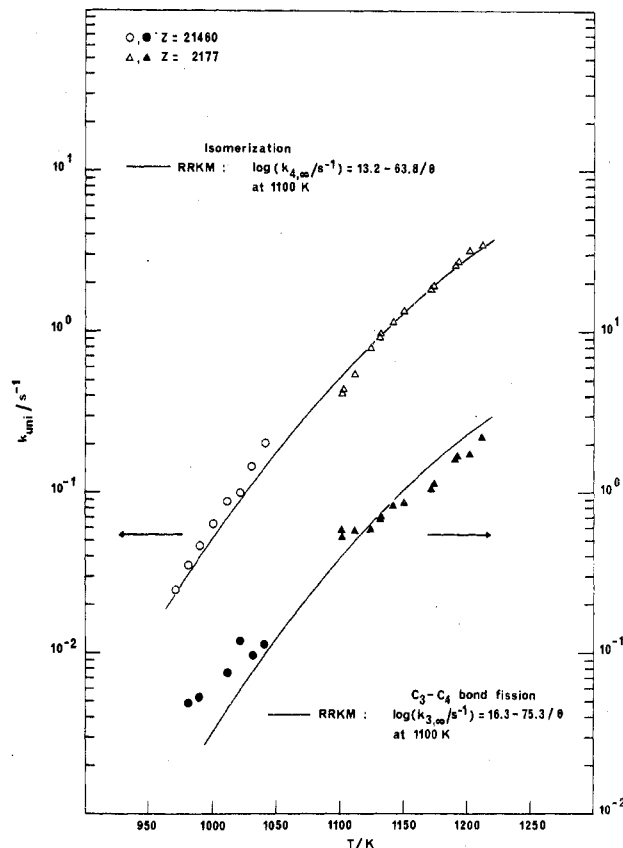TABLE II: Molecular Parameters in RRKM Calculations for MBTD

	molecule	isomerization complex	bond-fission complex "vibration"	bond-fission complex "rotation"
frequencies (cm^{-1}) and degeneracies	3060 (2)	3030 (1)	3060 (2)	3060 (2)
	2950 (6)	2950 (6)	2950 (6)	2950 (6)
	1970 (1)	2200 (1)	1970 (1)	1970 (1)
	1460 (5)	1860 (1)	1460 (5)	1460 (5)
	1370 (2)	1460 (4)	1370 (2)	1370 (2)
	1290 (1)	1380 (2)	1290 (1)	1290 (1)
	1190 (1)	1300 (2)	1190 (1)	1190 (1)
	1040 (4)	1160 (3)	1040 (3)	1040 (3)
	860 (3)	990 (6)	860 (3)	860 (3)
	700 (1)	700 (1)	455 (1)	360 (1)
	500 (1)	300 (1)	335 (1)	260 (1)
	360 (1)	200 (3)	250 (1)	150 (1)
	260 (1)	60 (1)	135 (2)	
	200 (2)		40 (2)	
	150 (2)			
$10^{120}I_A I_B I_C{}^a/(\text{g cm}^2)^3$	0.1845 × 10^7	0.2138 × 10^7	0.1264 × 10^8	0.1264 × 10^8
$10^{40}I_r(\text{CH}_3 \cdots \text{C(CH}_3)\text{=C=CH}_2)^{\ddagger}/(\text{g cm}^2)$			4.57	4.57
$10^{80}I_1 I_2/(\text{g cm}^2)^2$				
methyl (two-dimensional)				(3.18)^2
allenyl (two-dimensional)				(189.06)^2
rpd^b		2	2	2
$I^{\ddagger}/I$			1.93	1.93
$S°_{300}/(\text{cal mol}^{-1}\,\text{K}^{-1})$	76.1	76.7	88.1	93.0

^{a} One external rotation was chosen to be active in the bond-fission complexes (see text). ^{b} Reaction path degeneracy.
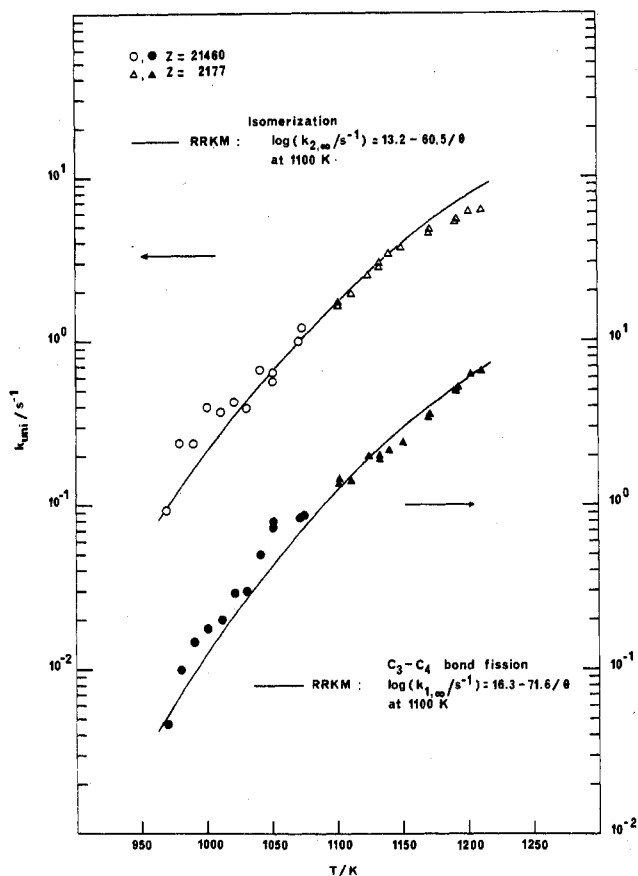
Figure 1. VLPP unimolecular rate constants for the two-channel decomposition of MBT: C_3–C_4 bond fission (filled symbols) and isomerization to MBTD (open symbols). The curves represent results of RRKM calculations. Note that each pathway has been assigned a different abscissa for clarity.

Figure 2. VLPP unimolecular rate constants for the two-channel decomposition of MBTD: C_3–C_4 bond fission (filled symbols) and isomerization to MBT (open symbols). The curves represent results of RRKM calculations. Note that each pathway has been assigned a different abscissa for clarity.

mated that the Arrhenius parameters for the formation of propyne from allene via cyclopropene are log (A/s^{-1}) = 13.05 and E = 63.70 kcal/mol. Thus, the estimated and observed rates for the overall reaction are not substantially different, and therefore the fine details of the mechanism

are unimportant in analyzing the VLPP data for the interconversion of MBT and MBTD (and the shock-tube data for the conversion of allene to propyne). Thus, in our RRKM calculations for the MBT $\rightleftharpoons$ MBTD system, we have used an A factor of $10^{13.2 \pm 0.6}$ s^{-1} based on the results of Lifshitz et al.[8]

TABLE III: Relevant Thermochemical Data[a]

species	$\Delta H_f{}^\circ{}_{300}$	$S^\circ{}_{300}$	$C_p{}^\circ$					
			300 K	500 K	900 K	1000 K	1100 K	1200 K
HC≡CCH(CH₃)₂[b,c]	32.6	76.4	25.1	36.2	50.1	52.4	54.5	56.4
H₂C=C=C(CH₃)₂[b,c]	31.0	76.6	25.3	36.0	50.0	52.4	54.5	56.2
HC≡CCH₂CH₃[b]	39.5	69.6	19.5	27.6	38.8	39.8		
H₃CC≡CCH₃[b]	35.0	67.8	18.7	26.4	37.4	39.3		
HC≡ĊH(CH₃)[d]	e	69.4	18.7	25.9	35.0	36.6	38.1	39.5
H₂C=C=ĊCH₃[d]	e	70.9	19.0	25.6	35.2	36.8	38.3	39.7
ĊH₃[f]	34.3	46.4	8.8	10.6	13.8	14.5	15.4	16.0
H[f]		52.1						

[a] $\Delta H_f{}^\circ$ in kcal/mol; S° and $C_p{}^\circ$ in cal mol^{-1} K^{-1}. [b] See ref 34. [c] Extrapolated values for $C_p{}^\circ$ at 1100 and 1200 K. [d] S° and $C_p{}^\circ$ were estimated by the difference method.[31] [e] Present work; see text. [f] See ref 32.

Details of the molecular and transition-state parameters employed in the RRKM calculations for MBT and MBTD are given in Tables I and II and in the Appendix. The RRKM rate constants are compared with the experimental results in Figures 1 and 2. In these calculations the gas/wall collision efficiency, β_w, was taken to be less than unity and assumed to decline with increase in temperature over the observed range as found in VLPP and VEM (variable encounter method) studies of similar molecules.[22,23,27-30] The values used were 0.76 at 950 K falling linearly to 0.22 at 1250 K.[22,23,29] The activation energies were found to differ by ≲1.5 kcal/mol from those based on $\beta_w = 1$, which is consistent with previous findings.[7,23]

In the RRKM calculations for the bond-fission pathways, the calculated rate constants for the hindered rotational transition-state model were essentially the same as those obtained by using the vibrational model for the same set of Arrhenius parameters (at 1100 K). This is in agreement with previous calculations.[22,23] The hindrance parameter η, which is a measure of the extent to which a fragment rotation in the transition state is hindered because of the presence of the other fragment,[20] was chosen such that it gave the selected A factor at 1100 K and was fixed at this value throughout the temperature range studied. η was found to be 92.3% for MBT and 71.6% for MBTD. For 3,3-dimethylbut-1-yne, revised calculations using the same hindered rotational model and log (A/s^{-1}) = 16.5 at 1100 K lead to η = 97.9%. In terms of the transition-state fragment structure, it seems reasonable that this value is greater than η for MBT, but the value for MBTD is rather low. However, as already noted in the case of the unusually low value of η for 4-methylpent-2-yne,[7] it is important to bear in mind that the exact relationship between η and the geometric parameters of the fragments in the transition state is unknown.

The high-pressure rate expressions at 1100 K thus obtained are as follows:

$$\log k_1 = (16.3 \pm 0.3) - (71.6 \pm 1.0)/\theta$$

$$\log k_2 = (13.2 \pm 0.6) - (60.5 \pm 1.0)/\theta$$

for MBT, and

$$\log k_3 = (16.3 \pm 0.3) - (75.3 \pm 1.0)/\theta$$

$$\log k_4 = (13.2 \pm 0.6) - (63.8 \pm 1.0)/\theta$$

for MBTD. The uncertainties in A_∞ are taken to be those suggested by Tsang[5] for bond fission and by Lifshitz et al.[8] for isomerization. The uncertainties in the activation energies were determined by the scatter of experimental data, together with the stated uncertainties in A_∞.

Discussion

Decomposition of MBT and MBTD via C_3–C_4 Bond Fission. The high-pressure activation energies for bond fission can be used to derive the heats of formation and resonance stabilization energies of the 1-methylpropargyl and 1-methylallenyl radicals. An assumption often used in conjunction with the vibrational transition-state model is that the reverse combination reaction has zero activation energy at the reaction temperature when the rate constant is measured in concentration units. This assumption has been used in related systems[1-3] and therefore will be employed in this work. However, the results are not significantly different if one uses the assumption that the reverse radical combination has zero activation energy at 0 K in conjunction with the rotational model for the transition state.[7,19]

For bond fission in MBT, $\Delta H°_{1100} = \Delta E°_{1100} + RT = 73.8$ kcal/mol. Combining this with the relevent thermochemical data given in Table III, we obtain $\Delta H_f°_{300}$-[HCCĊHCH₃] = 72.4 kcal/mol, which leads to $DH°_{300}$-[HCCCH(CH₃)–H] = 85.0 kcal/mol. Comparison with $DH°_{300}[(CH_3)_2CH–H] = 95$ kcal/mol[32] gives a value of 10.0 ± 2.2 kcal/mol for the resonance stabilization energy of the 1-methylpropargyl radical. Similarly, from the bond-fission data for MBTD, we obtain $\Delta H°_{1100} = 77.5$ kcal/mol, which leads to $\Delta H_f°_{300}$[H₂CCĊCH₃] = 74.3 kcal/mol. As noted earlier, this radical represents a resonance hybrid of two canonical forms, one propargyl and one allenyl

$$H_2\dot{C}C≡CCH_3 \leftrightarrow H_2C=C=\dot{C}CH_3$$
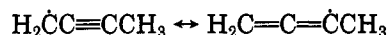
and the available experimental evidence[33] suggests that the former structure is thermodynamically more stable than the latter. As pointed out by Walsh,[35] the resonance stabilization energy of a propargylic radical may be based on either the propargyl structure or the allenyl structure, but the former is usually used.[36] Thus, combining the heat

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TABLE IV: Comparison of the Thermodynamic
Equilibrium Constant K for the Isomerization MBT
$\rightleftharpoons$ MBTD with the Rate-Constant Ratio, k_2/k_4,
at Selected Temperatures[a]

T/K	ΔH°_T	ΔS°_T	K	$k_{2,\infty}/ k_{4,\infty}$	$k_{2,\text{uni}}/ k_{4,\text{uni}}$
950	−1.7	−0.4	2.1	5.8	4.5
1000	−1.7	−0.4	2.0	5.2	4.0
1100	−1.7	−0.4	1.8	4.4	3.2
1200	−1.7	−0.4	1.7	4.0	2.6

[a] ΔH° in kcal/mol; ΔS° in cal mol^{-1} K^{-1}; k_{uni} and k_∞ in s^{-1}. K was calculated from $\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R$ where ΔH° and ΔS° were estimated from thermodynamic data listed in Table III.

of formation of the 1-methylallenyl/3-methylpropargyl radical with the heat of formation of but-2-yne leads to $DH^\circ_{300}[CH_3CCCH_2-H] = 91.4$ kcal/mol. The latter value when compared with $DH^\circ_{300}[CH_3CH_2CH_2-H] = 98$ kcal/mol[32] yields a value of 6.6 ± 2.2 kcal/mol for the resonance stabilization energy of the radical. The value obtained here for $\Delta H_f^\circ[H_2CCCCH_3]$ is in excellent agreement with the value of 73.6 kcal/mol obtained by Tsang[5] from the shock-tube pyrolysis of 6-methylhept-2-yne, but Tsang's value for the stabilization energy is 8.5 kcal/mol. The latter value was obtained from a combination of the activation energies for C–C fission in alkynes with the corresponding values for the alkanes and is consistent with $DH^\circ[n\text{-}C_3H_7-H] = 99.2$ kcal/mol (or $\Delta H_f^\circ(n\text{-}C_3H_7) = 22.2$ kcal/mol). Recent free-radical equilibrium studies[37] suggest that $\Delta H_f^\circ(n\text{-}C_3H_7) = 22.6$ kcal/mol, which confirms the value for $DH^\circ[n\text{-}C_3H_7-H]$ consistent with the shock-tube data. If this value is now adopted here, the present results lead to a resonance stabilization energy of 7.8 ± 2.2 kcal/mol. If one considers the experimental errors and the assumptions involved in the processing of the data, the present results are consistent with earlier VLPP[1-3,7] and shock-tube[5] studies of alkynes and further support our previous findings that methyl substitution does not have any significant effect on the propargyl resonance energy.[7]

MBT $\rightleftharpoons$ MBTD Interconversion. The rate of MBT → MBTD isomerization was observed to be faster than that of the reverse reaction throughout the temperature range studied. This is in contrast to the allene $\rightleftharpoons$ propyne system, where allene isomerization was found to be faster than that of propyne.[8] It should be noted that propyne is thermodynamically more stable than allene, whereas MBTD is more stable than MBT.[34] The activation energy for the isomerization of MBTD to MBT is in good

agreement with the value found by Lifshitz et al.[8] for the isomerization of allene to propyne. The experimental results indicate that methyl substitution does not have a significant effect on the rate.

The equilibrium constants for the MBT $\rightleftharpoons$ MBTD isomerization system can be evaluated from the ratio of the high-pressure rate constants for the forward and reverse reactions, $k_{2,\infty}/k_{4,\infty}$. These can be compared with the values estimated from known thermodynamic data. The comparison is shown in Table IV along with the ratios of the two rate constants in the VLPP falloff regime. When the uncertainty limits involved[38] are considered, the quantitative agreement between the observed and estimated values is reasonable. Qualitatively, the experimental results also show good agreement with the temperature dependence obtained from thermodynamic data, which indicates an equilibrium in favor of MBTD formation throughout the experimental temperature range.

Appendix

Molecular and Activated Complex Models. The vibrational frequency assignments of MBT were based on the frequencies reported for acetylene[39] and the isopropyl group,[40] and those of MBTD were according to the report of Harris and Longshore[41] but with some minor changes of the low frequencies. The two methyl internal rotations were treated as torsions. The moments of inertia of the molecules were calculated by using normal values for bond distances, bond angles, and atomic weights. They were found to agree well with previously reported values.[42] The calculated molecular entropies at 300 K agree with the values listed by Stull et al.[34]

In the vibrational model for the bond-fission activated complex for MBT, the C_3–C_4 bond stretch at 980 cm^{-1} was chosen as the reaction coordinate, and this bond was lengthened to 0.385 nm (i.e., 2.5 times the ground-state distance). The torsion mode of the leaving methyl group (200 cm^{-1}) was changed to a free rotation. Two $C_1\equiv C_2$–C_3 bending modes (510 and 240 cm^{-1}) were increased to 122% of their molecular values to account for resonance stiffening. Three low-frequency bending vibrations (3 × 340 cm^{-1}) and a rocking mode associated with the leaving methyl group were lowered to 27% of their molecular values. The external rotation about the —C≡C— axis was made active to allow this rotational mode to share in the random distribution of molecular energy.

In the rotational model for MBT, the four bending modes which were to become loosened in the vibrational model were changed to two two-dimensional hindered rotations of the two radical fragments. The two $C_1\equiv C_2$–C_3 bending modes retained their molecular frequencies. All other molecular parameters were the same as for the vibrational model.

The bond-fission activated complexes for MBTD using the vibrational and rotational models were set up in a similar manner as for MBT.

(36) In one case the appropriate C–H bond energy in the alkyne is compared with the standard C_{sp^3}–H bond energy, and in the other case the appropriate C–H bond energy in the allene is compared with the standard C_{sp^2}–H bond energy. It is important to realize that the resultant values for the stabilization energy will be different because of the different π bond systems of alkynes and allenes. A comparison cannot be made in this case because there is no information as to what a standard secondary C_{sp^2}–H bond energy should be. The standard primary C_{sp^2}–H bond energy (as in C_2H_4) is available only as a lower limit of 108 kcal/mol, a figure based on very limited, unpublished experimental data (Golden, D. M.; Benson, S. W. *Chem. Rev.* 1969, *69*, 125). However, in terms of the operational definition of resonance stabilization energy proposed by Benson[32] and confirmed by Rodgers et al. (Rodgers, A. S.; Wu, M. C. R.; Kuitu, L. *J. Phys. Chem.* 1972, *76*, 918) as the "best" approach, the C–H bond energy in the diene should be compared with the appropriate standard C–H bond energy in the fully saturated compound and not with that in the olefin. Thus combining $\Delta H_f^\circ[H_2CCCCH_3]$ with the heat of formation of buta-1,2-diene[34] leads to $DH^\circ_{300}[H_2CCC(CH_3)-H] = 87.6$ kcal/mol, which, when compared with $DH^\circ_{300}[H_3CCH_2CH(CH_3)-H] = 96.1$ kcal/mol (calculated from $\Delta H_f^\circ(n$-butane)[32] and $\Delta H_f^\circ(sec$-butyl radical) (Marshall, R. M.; Page, N. D. *Int. J. Chem. Kinet.* 1979, *11*, 199) leads to a stabilization energy of 8.5 kcal/mol, in good agreement with the value obtained by using the derived bond energy in but-2-yne.
(37) Marshall, R. M.; Rahman, L. *Int. J. Chem. Kinet.* 1977, *9*, 705.

(38) The uncertainty limits in the calculated values come from the experimental activation energies, which are known to ±1.0 kcal/mol. The main source of error involved in the estimated values comes from the enthalpy terms, which are known to ±1.0 kcal/mol.
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For the isomerization pathway, the activated complex was set up according to the 1,3 hydrogen-shift mechanism proposed by Lifshitz et al.[8] This is not an endorsement of the mechanism; it merely provides us with a procedure for estimating a set of transition-state frequencies. One of the C$\cdots$H liasons was chosen to be the reaction coordinate. The C$\rightleftharpoons$C and C$\rightharpoondown$C distances were assumed to have values intermediate between the C$\equiv$C and C$=$C, and C$=$C and C—C bond lengths, respectively. The C$\cdots$H distance was assumed to have the normal C–H bond length. Assignments of frequencies for partial bond bending and stretching were adopted from Benson.[32]

Rate Coefficient for the Reaction of CH$_3$O$_2$ with NO at 295 K

I. C. Plumb, K. R. Ryan, *

CSIRO, Division of Applied Physics, Sydney, Australia 2070

J. R. Steven, and M. F. R. Mulcahy

Fuel and Atmospheric Science Section, CSIRO, Division of Fossil Fuels, North Ryde, New South Wales, Australia 2113
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The rate coefficient for the reaction of CH$_3$O$_2$ with excess NO has been measured in helium at 295 K by using discharge flow/mass spectrometry to monitor the CH$_3$O$_2$. Two flow tubes, one of 1.00-cm i.d. and the other of 2.18-cm i.d., were used. The results from both tubes agree, within experimental error, giving a value for the rate coefficient of $(8.6 \pm 2.0) \times 10^{-12}$ cm^3 s^{-1}.

Introduction

Interest in the gas-phase reactions of CH$_3$O$_2$ stems from the fact that this species plays an important role in both atmospheric and combustion chemistry. In the chemistry of the troposphere, the oxidation of NO to NO$_2$ by reaction 1 is an important step in the formation of ozone. Until

$$NO + CH_3O_2 \rightarrow NO_2 + CH_3O \qquad (1)$$
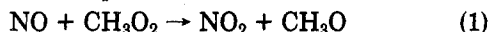
recently, only indirect methods have been used to measure the rate coefficient k_1 for reaction 1, and the estimates so obtained have varied widely.[1-5]

A value of $(8 \pm 2) \times 10^{-12}$ cm^3 s^{-1} for k_1 obtained by direct measurement of the consumption of CH$_3$O$_2$ using discharge flow/mass spectroscopy (DF/MS) was reported recently from this laboratory.[6] Since then, other direct measurements have been made by modulated molecular spectroscopy (MMS)[7] and by flash photolysis/ultraviolet absorption (FP/UV).[8,9] The results of these measurements are shown in Table I.

In our previous study, CH$_3$O$_2$ was produced by reactions 2 and 3 and then allowed to react with NO. The rate

$$O + C_2H_4 \rightarrow CH_3 + CHO \qquad (2)$$

$$CH_3 + O_2 \xrightarrow{M} CH_3O_2 \qquad (3)$$
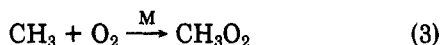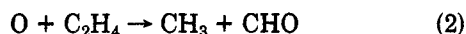
coefficient was determined in two ways. In one set of experiments, the reaction time was varied by moving the NO inlet along the flow tube while keeping [NO] fixed. In the other, the NO inlet position, hence the reaction time,

TABLE I: Summary of Rate Coefficients for Reaction 1

$10^{12}k_1$,^{a} cm^3 s^{-1}	exptl method	ref	$10^{12}k_1$,^{a} cm^3 s^{-1}	exptl method	ref
8 ± 2	DF/MS	6	3 ± 0.2	FP/UV	8
6 ± 2	MMS	7	7.1 ± 1.4	FP/UV	9

^{a} Measured value.

was fixed and the [NO] was varied. In computing k_1, we assumed that negligible consumption of NO occurred and that, for those experiments in which the reaction time was varied, the pseudo-first-order decay coefficient k_ψ was related to k_1 by

$$k_\psi = k_1[NO]$$

This relationship was found to hold experimentally for [NO] ranging from 4×10^{12} to 31×10^{12} cm^{-3}.

Sander and Watson[9] have criticized this work, arguing that the model used in considering the production of CH$_3$O$_2$ was too simple. Partly as a result of this, they suggest that, for the lowest [NO] employed, almost 60% of the NO would have been consumed at the $1/e$ point for CH$_3$O$_2$ and that this would have led to a value of k_1 too low by $\sim$25%. In fact, we had carried out substantial modeling of the system, with up to 89 possible reactions included in the model, although only the main loss processes of CH$_3$ and O were referred to specifically in our paper.[6]

Basically, the results of our modeling agree with those obtained by Sander and Watson.[9] Experimentally, however, we find that, when [NO] = 5×10^{12} cm^{-3} (that is, at the low end of the range of [NO] used), $\sim$20% of the NO is consumed at the $1/e$ point for CH$_3$O$_2$ and not 60% as predicted. This experimental result would yield a value for k_1 $\sim$10% low under these conditions, but significantly closer to the true value at higher [NO].

In view of the importance of reaction 1 and the criticism referred to above, we have remeasured k_1. In this new work, we have used a more straightforward method for producing CH$_3$O$_2$ than in our previous work.

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