The energy of activation of CH_{3} radical rupture from the radical \((\text{CH}_{3})_{2}\text{CCH(CH}_{3})_{2}\) is 142.2 kJ mol^{-1}; the self-combination rate constant is \(k_{c}(\text{CH}_{3})_{2}\text{CCH(CH}_{3})_{2}\) = 10^{7.3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.

Энергия активации отщепления радикала CH_{3} от радикала \((\text{CH}_{3})_{2}\text{CCH(CH}_{3})_{2}\) равна 142,2 кДж/моль, а константа скорости реакции соединения радикалов \(k_{c}(\text{CH}_{3})_{2}\text{CCH(CH}_{3})_{2}\) = 10^{7.3} \text{ дм}^3 \text{ моль}^{-1} \text{ сек}^{-1}.

Unimolecular decomposition reactions of primary, secondary and tertiary alkyl radicals to yield the CH_{3} radical and a terminal or a non-terminal olefin are of major importance in the thermal decomposition of organic compounds. In spite of this, most studies relate to the decompositions of small primary radicals, i.e. 1-propyl, 2-methylpropyl and 2,2-dimethylpropyl [1-5], to yield terminal olefins. The only secondary radical whose decomposition has been studied is 2-butyl [5], and the rate constant of the decomposition of a tertiary radical, \((\text{CH}_{3})_{2}\text{CCH(CH}_{3})_{2}\) (23DMB2·), was also determined recently [6]. With the assumption that \(A_5 = 10^{13.8} \text{ s}^{-1} \pm 0.5 [6]\), it was estimated that \(E_5 = 129.5 \pm 7 \text{ kJ mol}^{-1}\). The only suggestion for...
this reaction to have a higher energy of activation was made in a critical data evaluation by Warnatz [7].

A detailed kinetic study of the products of thermal decomposition of azosiopropane in a conventional grease-free static system, using end-product analysis, has revealed the formation of decomposition products of the radical 23DMB2- and for the first time yielded Arrhenius parameters on the decomposition.

RESULTS AND DISCUSSION

The reaction was performed in a static system at 12 temperatures in the range of 466-540 K. The apparatus and the experimental procedure applied were similar to those described earlier [8].

The radical 23DMB2- was formed in situ in the thermal decomposition of azoisopropane from the cross-combination product of the dominant radicals:

\[
(CH_3)_2CH(N=C(N(CH_3))_2 \rightarrow N_2 + 2 \text{2-C}_3\text{H}_7
\]

\[
2\text{C}_3\text{H}_7^- + (CH_3)_2CH(N=C(N(CH_3))_2 \rightarrow C_3H_8 + (CH_3)_2CN=NCH(CH_3)_2
\]

\[
2\text{C}_3\text{H}_7^- + (CH_3)_2CN=NCH(CH_3)_2 \rightarrow (CH_3)_2CHC(CH_3)_2N=NCH(CH_3)_2
\]

\[
(CH_3)_2CHC(CH_3)_2N=NCH(CH_3)_2 \rightarrow (CH_3)_2CN=NCH(CH_3)_2 + N_2 + 2\text{C}_3\text{H}_7^-.
\]

The unimolecular decomposition

\[
(CH_3)_2\overset{.}{C}CH(CH_3)_2 \rightarrow (CH_3)_2C=CH(CH_3)(2MB2) + CH_3.
\]

was assumed to be the only source of 2MB2. The rate of formation of this product is given by

\[r(2MB2) = k_3[23DMB2^-]\]

The concentration of the radical was eliminated via the measured combination products

\[
2\text{C}_3\text{H}_7^- + (CH_3)_2\overset{.}{C}CH(CH_3)_2 \rightarrow (CH_3)_2CHC(CH_3)_2CH(CH_3)_2(2334\text{TMPa})
\]

\[
2\text{C}_3\text{H}_7^- + 2\text{C}_3\text{H}_7^- \rightarrow (CH_3)_2CHCH(CH_3)_2 (23\text{DMBa})
\]