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# THERMAL DEGRADATION OF POLYISOBUTYLENE STUDIED USING FACTOR-JUMP THERMOGRAVIMETRY

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The overall activation energy of the thermal degradation of polyisobutylene has been measured using factor-jump thermogravimetry to be 206 ± 1 kJ/mole over the range 365 to 405° in $N_2$ at 800 mm Hg pressure and flowing at 4 mm/s over the sample. This is consistent with some values reported for thermal degradation in vacuum and in solution. In 5 mm Hg of $N_2$, an apparent activation energy of 218 ± 2 kJ/mole was found, and in vacuum the apparent activation energy is 238 ± 13 kJ/mole. Troublesome bubbling made the vacuum values difficult to measure. Substitution of reasonable values for the activation energies of initiation, $E_i$, termination, $E_t$, and the activation energy, $E_a$, for vacuum degradation in the equation $E_a = E_i/2 + E_d - E_t/2$ yields an activation energy $E_d = 84$ kJ/mole for the unzipping reaction. This equation presupposes a degradation mechanism of random initiation, unzipping, and bimolecular termination. Substitution of reasonable values for the heat of polymerization, $\Delta H$, in the definition $\Delta H = E_p - E_d$ suggests that the activation energy of the polymerization reaction at 375° is approximately 30 kJ/mole.

Polyisobutylene (PIBu) has the formula $-[C(CH_3)_2-CH_2]_n-$ and hence ideally contains no tertiary carbon atoms. Its thermal degradation in vacuum was studied by Madorsky and coworkers [1], who heated samples of PIBu to temperatures between 313 and 460° and used mass spectrometry to characterize the fraction of degradation products volatile above − 70°. Typically, this was 20 percent of the volatiles and was stated to consist of almost entirely of isobutylene. About 10 percent of the volatiles were thought to be dimer and trimer. The remaining 70 percent of the volatile material was assumed to be higher oligomers, with an average length of 9 to 10 monomer units. Earlier, Wall [2] had reported that 78 percent of the volatile products consisted of monomer when the decomposition was carried out at 400°. Using thermogravimetry to measure rates of volatilization at various temperatures in the range 306° to 326°, Madorsky and Straus [3] determined the activation energy of the in vacuo thermal degradation to be 49 kcal/mol (200 kJ/mole).

Inoue et al. [4] reported an activation energy of initiation of 41 kcal/mole (170 kJ/mole) and an average chain length of 30 for thermal degradation of PIBu above 280°. Slobodin and Matusevich [5] found the products of PIBu which had been decomposed thermally at 325 to 400° to be 49 percent isobutylene, ~ 1 percent isobutene and isopentane, 17 percent $C_8$ hydrocarbons, 18 percent $C_{12}$ hydrocarbons, 8 percent $C_{16}$ hydrocarbons, 2 percent $C_{20}$ hydrocarbons and 3 percent $C_{24}$ hydrocarbons.

McIntyre et al. [6] examined the thermal degradation of fractioned PIBu at 299° and found that after ~ 30 percent of reaction all fractions degraded at the same rate. The rapid change in molecular weight with extent of reaction was used to show that initiation was random rather than end initiated.

McGuchan and McNeill [7] in general confirmed the observations of McIntyre et al. [6]. The degradation rate was found to decrease continuously with percent degradation for all molecular weights studied. The degradations were carried out at 310°, and the rate was estimated from the pressure of volatiles.

Tsuchiya and Sumi [8] analyzed the products of thermal degradation using gas and liquid phase chromatography. Conditions were similar to those of Madorsky and Straus [3]. The mole percentages of isobutylene in the volatile fractions were 64 percent at 325°, 79 percent at 345° and 82 percent at 365°. Using the formulae and quantities given in their Table IV, we estimate the value at 365° to correspond to ~ 75 percent by weight isobutylene, which is in good agreement with the findings of Wall [2].

The mechanism of degradation was further examined by Seeger and Cantow [9], who used gas chromatography to identify the deliberately hydrogenated products of PIBu pyrolysed at 800°. The pyrolysis yield was mostly monomer, although fragments up to the octamer were detected.

Sadykhov [10] examined the thermal degradation of PIBu alone and mixed with various other vinyl polymers. The aim was to improve the properties of PIBu when used as a thickening agent in mineral oils. Bulk degradation of PIBu were carried out at 250° in quartz vessels. Products were analyzed chromatographically. Random scission was indicated by the dependence of degradation rates on $\bar{M}_n^2$, where $\bar{M}_n$ is the number average molecular weight of the polymer. An activation energy of 48.4 kcal/mole (202 kJ/mole) was found.

In the cited references, there is agreement that a mechanism consistent with the experimental results includes scission of the $-C-C$ backbone as the initiating step. The resulting tertiary radical can only unzip or transfer; backbiting is very unlikely because the fifth carbon atom in the backbone is quaternary. The primary radical can unzip, transfer, and back-bite, but even there, backbiting is apparently not very important, probably because the hydrogen to be abstracted is on a secondary carbon atom. Because no "reactive" hydrogens are available (i.e., H bonded to a tertiary carbon atom) and because the hydrogens in $-CH_2-$ are sterically protected by the neighboring $-C(CH_3)_2-$ groups, back-biting and intermolecular transfer are minor reactions. Disproportionation of radicals to give $-CH{=}C(CH_3)_2$ and $CH_3-C(CH_3)_2-CH_2-$ groups is usually suggested as the main termination step.

## Experimental

Approximately 15 mg samples of PIBu (molecular weight 125.000, obtained from Polyscience, Inc.) were subjected to factor-jump thermogravimetry [11, 12] in $N_2$ flowing at 4 mm/s at 800 mm Hg* pressure, at 5 mm Hg pressure and in vacuum. 'Factor-jump' refers here to sudden changes in a rate-determining variable. The polymer was subjected to a series of isothermals 5 to 10° apart, ~ 10 minutes in duration, and alternately higher and lower in temperature. The specimen weight and temperature were recorded continually. Both the rates of weight loss and the temperatures in adjacent isothermals were extrapolated in terms of time to halfway between the end of the earlier isothermal and the beginning of the later isothermal. An equilibration time of ~ 3½ minutes was allowed after a change in temperature. The extrapolations were over ~ 1% in terms of order of reaction. The activation energy, $E$, was estimated from the Arrhenius equation as

$$E = \left(\frac{RT_1T_2}{T_2 - T_1}\right) \ln\left(\frac{r_2}{r_1}\right)$$

where the $r$'s are the rates and the $T$'s the temperatures extrapolated from two adjacent isothermals and $R$ is the gas constant. Because these rates and temperatures are estimated for the same instant in time, and hence for the same extent of reaction, terms containing the extent of reaction cancel each other out [11]. The procedure used here was the same as that used to study the degradation of polystyrene [12], except that lower rates of weight loss were used at 5 mm Hg and in vacuum. The degradations in $N_2$ followed a smooth course and estimation of the activation energy presented no problems. In vacuum, bubbling in the sample made the sample weight unsteady and complicated the estimation of the activation energy. The experimental conditions and results are given in Tables 1 through 4.

## Results and discussion

Averages of the individual activation energies in Tables 1 through 4 are given in Table 5. The value for degradation in 800 mmHg measured here is 49.2 ±0.3 kcal/mole (206±1 kJ/mole). This is in good agreement with the values reported for degradation in vacuum in reference [3] and in solution in reference [10].

In 5 mm Hg, the apparent activation energy is 52.1 ±0.5 kcal/mole (estimated as being representative of the appropriate averages in Table 5), which corresponds to 218±2 kJ/mole.

For degradation in vacuum, the individual estimates of the activation energy were widely scattered, owing to the destabilizing effect of the unsteady sample weight on the rate of weight loss data. The apparent activation energy is ~ 57±3 kcal/mole

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* 1 mm Hg = 133 pascals

**Table 1** Apparent activation energy data for PIBu degrading in 99.95% $N_2$ at 800 mm Hg and flowing at 4 mm/s

| DOC | *E* | Sig *E* | *T*1 | *R*1 | *T*2 | *R*2 | SWT (*mg*) | %*R*1 | %*R*2 | *n* |
|---|---|---|---|---|---|---|---|---|---|---|
| 22 | 49.8 | 1.6[a] | 373.62 (1) | – 40.2 (4) | 366.63 (2) | – 26.3 (2) | 10.6 | 0 | – 3 | 0 |
| 28 | 47.5 | 1.0 | 366.78 (2) | – 25.3 (2) | 376.74 (1) | – 44.8 (3) | 9.8 | – 3 | – 6 | 0.4 |
| 38 | 50.2 | 1.0 | 376.65 (2) | – 41.9 (3) | 369.67 (2) | – 27.4 (1) | 8.4 | – 6 | – 9 | 0.9 |
| 44 | 48.2 | 0.5 | 369.72 (2) | – 25.1 (1) | 379.79 (2) | – 44.8 (1) | 7.6 | – 9 | – 13 | 0.7 |
| 53 | 47.6 | 0.7 | 379.67 (2) | – 39.1 (1) | 372.59 (2) | – 26.2 (1) | 6.3 | – 13 | – 15 | 1.3 |
| 59 | 49.6 | 0.5 | 372.85 (2) | – 22.5 (1) | 382.75 (1) | – 40.3 (1) | 5.6 | – 15 | – 18 | 0.8 |
| 67 | 50.1 | 0.6 | 382.65 (2) | – 33.4 (1) | 375.60 (1) | – 22.0 (1) | 4.4 | – 18 | – 15 | 1.1 |
| 72 | 47.6 | 0.5 | 375.81 (2) | – 18.8 (1) | 385.76 (2) | – 32.9 (1) | 3.8 | – 15 | – 25 | 0.9 |
| 78 | 48.3 | 0.7 | 385.66 (2) | – 25.5 (1) | 378.62 (1) | – 17.1 (1) | 2.9 | – 25 | – 23 | 1.2 |
| 82 | 48.5 | 0.3 | 378.69 (2) | – 13.5 (1) | 396.69 (2) | – 36.7 (1) | 2.3 | – 23 | – 57 | 1.1 |
| 90 | 45.2 | 0.8 | 366.43 (1) | – 20.2 (1) | 389.60 (2) | – 14.3 (1) | 1.3 | – 57 | 0 | 0 |
| 12 | 52.5[b] | 0.7 | 356.98 (2) | – 12.5 (2) | 374.91 (2) | – 39.9 (3) | 11.2 | 0 | 0 | 0 |
| 23 | 51.1 | 0.9 | 374.81 (2) | – 39.6 (2) | 367.75 (2) | – 25.6 (1) | 9.8 | 0 | – 6 | 0.9 |
| 29 | 49.3 | 0.5 | 367.89 (2) | – 24.0 (1) | 377.93 (2) | – 43.6 (1) | 9.0 | – 6 | – 9 | 0.6 |
| 39 | 49.6 | 0.6 | 377.69 (2) | – 39.5 (1) | 370.77 (2) | – 26.1 (1) | 7.8 | – 9 | – 9 | 0.9 |
| 45 | 49.0 | 0.5 | 370.85 (2) | – 23.9 (1) | 380.86 (2) | – 42.9 (1) | 7.0 | – 9 | – 14 | 0.7 |
| 55 | 51.2 | 0.7 | 380.70 (2) | – 37.1 (1) | 373.57 (3) | – 24.0 (1) | 5.7 | – 14 | – 7 | 0.7 |
| 60 | 47.0 | 0.5 | 373.94 (3) | – 22.4 (1) | 383.81 (2) | – 38.8 (1) | 5.0 | – 7 | – 19 | 0.8 |
| 69 | 49.5 | 0.8 | 383.70 (2) | – 31.9 (1) | 376.69 (4) | – 21.2 (1) | 3.9 | – 19 | – 17 | 1.1 |
| 74 | 48.0 | 0.6 | 376.88 (4) | – 17.7 (1) | 386.75 (3) | – 30.8 (1) | 3.3 | – 17 | – 26 | 0.9 |
| 80 | 50.4 | 0.8 | 386.77 (3) | – 23.5 (1) | 379.88 (4) | – 15.7 (1) | 2.4 | – 26 | – 22 | 0.9 |
| 84 | 48.1 | 0.4 | 379.73 (4) | – 12.6 (1) | 397.68 (2) | – 33.9 (2) | 1.9 | – 22 | – 62 | 1.0 |
| 91 | 40.9[b] | 1.2 | 397.51 (2) | – 17.7 (1) | 390.66 (2) | – 12.9 (1) | 1.0 | – 62 | 0 | 0 |
| 16 | 50.8 | 1.0 | 363.78 (5) | – 28.4 (1) | 356.75 (5) | – 18.2 (1) | 12.1 | 0 | – 2 | 0 |
| 20 | 48.2 | 0.7 | 356.90 (5) | – 17.7 (1) | 366.83 (5) | – 32.2 (1) | 11.5 | – 2 | 0 | 0 |
| 27 | 48.9 | 0.9 | 366.73 (5) | – 32.0 (1) | 359.82 (4) | – 21.0 (1) | 10.5 | 0 | – 6 | 1.0 |
| 31 | 47.8 | 0.6 | 359.79 (4) | – 19.7 (1) | 369.74 (5) | – 35.4 (1) | 9.9 | – 6 | – 3 | 0.4 |
| 39 | 49.2 | 0.7 | 369.88 (5) | – 34.1 (1) | 362.70 (4) | – 22.2 (1) | 8.8 | – 3 | – 6 | 1.0 |
| 43 | 48.6 | 0.5 | 362.92 (4) | – 20.8 (1) | 372.89 (5) | – 37.6 (1) | 8.2 | – 6 | – 9 | 0.5 |
| 51 | 48.4 | 0.9 | 372.68 (5) | – 34.3 (1) | 365.79 (4) | – 22.9 (1) | 7.0 | – 9 | – 11 | 1.1 |
| 56 | 48.1 | 0.6 | 365.75 (4) | – 20.4 (1) | 375.90 (3) | – 36.9 (1) | 6.4 | – 11 | – 15 | 0.7 |

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|---|---|---|---|---|---|---|---|---|---|---|
| 63 | 46.6 | 0.8 | 375.59 (3) | − 31.6 (1) | 368.78 (5) | − 21.6 (1) | 5.3 | − 15 | − 17 | 1.4 |
| 67 | 49.2 | 0.6 | 368.71 (5) | − 18.2 (1) | 378.79 (6) | − 33.0 (1) | 4.7 | − 17 | − 18 | 0.8 |
| 74 | 48.6 | 0.8 | 378.68 (6) | − 27.5 (1) | 371.59 (6) | − 18.2 (1) | 3.7 | − 18 | − 13 | 1.0 |
| 77 | 47.8 | 0.6 | 371.94 (6) | − 15.9 (1) | 381.95 (5) | − 28.2 (1) | 3.2 | − 13 | − 26 | 0.9 |
| 83 | 46.0 | 0.8 | 381.69 (5) | − 21.6 (1) | 374.89 (5) | − 14.9 (1) | 2.4 | − 26 | − 25 | 1.1 |
| 86 | 49.3 | 0.4 | 374.75 (6) | − 11.6 (1) | 392.79 (7) | − 32.7 (1) | 2.0 | − 25 | − 53 | 0.9 |
| 92 | 47.8 | 0.9 | 392.65 (6) | − 18.8 (1) | 385.63 (4) | − 12.8 (1) | 1.1 | − 53 | 0 | 0 |
| 12 | 48.8 | 1.1 | 368.61 (6) | − 29.7 (1) | 361.72 (7) | − 19.6 (1) | 12.0 | 0 | − 6 | 0 |
| 17 | 50.4 | 0.7 | 361.73 (7) | − 18.4 (1) | 371.84 (3) | − 34.4 (1) | 11.4 | − 6 | − 5 | 0.4 |
| 24 | 48.3 | 0.8 | 371.50 (3) | − 32.5 (1) | 364.66 (4) | − 21.7 (1) | 10.4 | − 5 | − 6 | 0.9 |
| 29 | 48.7 | 0.6 | 364.59 (4) | − 20.4 (1) | 374.71 (5) | − 37.2 (1) | 9.7 | − 6 | − 6 | 0.6 |
| 37 | 47.6 | 0.7 | 374.77 (5) | − 34.7 (1) | 367.58 (4) | − 22.9 (1) | 8.6 | − 6 | − 7 | 1.0 |
| 42 | 50.3 | 0.6 | 357.78 (4) | − 21.3 (1) | 377.72 (4) | − 39.0 (2) | 7.9 | − 7 | − 12 | 0.8 |
| 50 | 47.4 | 0.9 | 377.63 (5) | − 34.4 (2) | 370.54 (5) | − 23.0 (1) | 6.8 | − 12 | − 10 | 1.1 |
| 55 | 48.1 | 0.6 | 370.73 (5) | − 20.7 (1) | 380.68 (5) | − 36.8 (1) | 6.1 | − 10 | − 16 | 0.8 |
| 63 | 50.2 | 0.9 | 380.60 (5) | − 31.0 (1) | 373.58 (4) | − 20.4 (1) | 5.1 | − 16 | − 9 | 0.8 |
| 67 | 46.5 | 0.5 | 373.67 (4) | − 18.4 (1) | 383.75 (5) | − 32.1 (1) | 4.5 | − 9 | − 20 | 0.8 |
| 74 | 47.5 | 1.0 | 383.33 (4) | − 26.1 (1) | 376.51 (5) | − 17.8 (1) | 3.6 | − 20 | − 20 | 1.2 |
| 78 | 49.5 | 0.5 | 376.60 (7) | − 14.6 (1) | 394.52 (6) | − 40.8 (1) | 3.0 | − 20 | − 44 | 9.2 |
| 86 | 45.3 | 0.8 | 394.61 (5) | − 26.1 (1) | 387.51 (4) | − 18.1 (1) | 1.8 | − 44 | − 42 | 1.3 |
| 90 | 48.5 | 0.4 | 387.59 (4) | − 11.7 (1) | 405.42 (4) | − 30.9 (1) | 1.3 | − 42 | 0 | 0 |

DOC = percent degree of conversion or percent extent of reaction; $E$ = apparent activation energy in kcal/mole; sig $E$ = estimated standard deviation of $E$; $T1$ = temperature in °C at which rate of weight loss $R1$ was obtained. $T2$ and $R2$ are similarly related; $R1$, $R2$ = rates of weight loss in μv/s, where 20 μv corresponds to 1 μg; SWT = sample weight in mg; %$R1$, %$R2$ = 100 (initial rate-final rate)/(average rate) for isothermals 1 and 2, respectively, value of zero means *one of rates is not available in table*; $n = [\ln (R_1 e^{E/RT_1}/R_2 e^{E/RT_2})]/\ln(\mathrm{SWT}_1/\mathrm{SWT}_2)$, where $n$ is an apparent order of reaction. Only data with $40 < \mathrm{DOC} < 90$ used for averaging purposes; $a$ = discarded in probability plot: sig $E$ value too extreme; $b$ = discarded in probability plot: $E$ value too extreme.

**Table 2** Apparent activation energy data for PIBu degrading in 99.95% $N_2$ at 800 mm Hg flowing at 4 mm/s

| DOC | *E* | Sig *E* | *T*1 | *R*1 | *T*2 | *R*2 | SWT (mg) | %*R*1 | %*R*2 | *n* |
|---|---|---|---|---|---|---|---|---|---|---|
| 9 | 50.0 | 1.7 | 369.60 (3) | − 21.1 (2) | 363.56 (2) | − 14.6 (1) | 12.5 | 0 | 2 | 0 |
| 13 | 49.3 | 0.6 | 363.89 (3) | − 14.9 (1) | 379.89 (6) | − 38.6 (2) | 11.9 | 2 | − 4 | 0.2 |
| 23 | 49.7 | 1.0 | 379.59 (5) | − 37.1 (1) | 373.56 (2) | − 26.0 (1) | 10.5 | − 4 | − 7 | 1.0 |
| 29 | 51.2 | 0.7 | 373.70 (2) | − 24.1 (1) | 381.85 (3) | − 39.5 (1) | 9.6 | − 7 | 0 | 0 |
| 61 | 49.6 | 0.3 | 375.76 (3) | − 16.3 (1) | 391.85 (3) | − 41.2 (1) | 5.3 | 0 | − 28 | 0 |
| 70 | 49.1 | 0.7 | 391.49 (2) | − 30.8 (1) | 383.56 (1) | − 22.1 (1) | 4.0 | − 28 | − 21 | 1.2 |
| 75 | 49.2 | 0.5 | 385.68 (1) | − 17.9 (1) | 393.80 (2) | − 28.2 (1) | 3.3 | − 21 | − 28 | 1.0 |
| 81 | 52.3 | 0.7 | 393.53 (2) | − 21.1 (1) | 387.49 (2) | − 14.7 (0) | 2.5 | − 28 | − 24 | 1.2 |
| 85 | 49.1 | 0.3 | 387.74 (3) | − 11.5 (1) | 403.56 (4) | − 27.6 (1) | 2.0 | − 24 | 0 | 0 |
| 20 | 51.0 | 0.6 | 381.43 (4) | − 36.5 (1) | 389.73 (4) | − 59.7 (1) | 8.1 | 0 | − 19 | 0 |
| 38 | 50.1 | 0.6 | 389.42 (4) | − 49.0 (1) | 383.33 (2) | − 34.4 (1) | 6.3 | − 19 | − 15 | 0.9 |
| 48 | 49.8 | 0.4 | 383.61 (2) | − 29.4 (1) | 391.71 (3) | − 46.8 (1) | 5.2 | − 15 | − 25 | 0.8 |
| 62 | 55.6[a] | 0.6 | 391.47 (3) | − 36.3 (1) | 385.39 (2) | − 24.6 (1) | 3.8 | − 25 | − 18 | 0.9 |
| 69 | 47.6 | 0.4 | 385.66 (2) | − 20.4 (1) | 393.64 (3) | − 31.6 (1) | 3.1 | − 18 | − 33 | 0.9 |
| 78 | 47.7 | 0.7 | 393.49 (3) | − 22.5 (1) | 387.46 (3) | − 16.2 (1) | 2.1 | − 33 | − 30 | 1.1 |
| 84 | 50.1 | 0.4 | 387.58 (3) | − 11.9 (1) | 403.60 (6) | − 29.4 (1) | 1.6 | − 30 | 0 | 0 |
| 8 | 49.9 | 1.5 | 361.66 (3) | − 15.0 (2) | 369.71 (2) | − 24.6 (2) | 10.2 | 0 | 0 | 0 |
| 15 | 50.2 | 1.5 | 369.54 (2) | − 24.8 (2) | 363.54 (3) | − 17.1 (1) | 9.4 | 0 | − 5 | 1.1 |
| 20 | 49.9 | 0.9 | 363.70 (2) | − 16.2 (1) | 371.74 (2) | − 26.5 (1) | 8.8 | − 5 | − 6 | 0.5 |
| 28 | 46.1 | 0.9 | 371.56 (3) | − 24.9 (1) | 365.49 (3) | − 17.7 (1) | 8.0 | − 6 | − 8 | 1.4 |
| 33 | 50.2 | 0.8 | 365.77 (3) | − 16.2 (1) | 373.77 (6) | − 26.5 (1) | 7.4 | − 8 | − 9 | 0.7 |
| 40 | 47.9 | 0.9 | 373.50 (6) | − 24.0 (1) | 367.54 (3) | − 17.0 (1) | 6.6 | − 9 | − 7 | 1.0 |
| 45 | 48.3 | 0.6 | 367.75 (3) | − 15.8 (1) | 375.79 (3) | − 25.2 (1) | 6.0 | − 7 | − 13 | 0.9 |
| 52 | 48.7 | 0.7 | 375.59 (3) | − 22.1 (1) | 369.50 (2) | − 15.4 (0) | 5.2 | − 13 | − 8 | 0.8 |
| 57 | 48.2 | 0.3 | 369.75 (2) | − 14.2 (1) | 385.79 (3) | − 35.5 (1) | 4.7 | − 8 | − 25 | 0.8 |
| 68 | 47.6 | 0.6 | 385.54 (3) | − 27.5 (1) | 379.55 (2) | − 19.7 (1) | 3.5 | − 25 | − 19 | 1.1 |
| 73 | 48.9 | 0.5 | 379.67 (2) | − 16.3 (1) | 387.70 (3) | − 25.7 (1) | 2.9 | − 19 | − 28 | 0.9 |
| 80 | 46.3 | 1.1 | 387.56 (3) | − 19.3 (1) | 381.46 (2) | − 13.9 (1) | 2.1 | − 28 | 0 | 0 |

Headings as in Table 1. Data rejected for DOC $< 40$, DOC $> 90$. [a] discarded by probability plot, $E_j$ too extreme.

**Table 3** Apparent activation energy data for PIBu degrading in 99.995% $N_2$ at 5 mm Hg

| DOC | *E* | Sig *E* | *T*1 | *R*1 | *T*2 | *R*2 | SWT (mg) | %*R*1 | %*R*2 | *n* |
|---|---|---|---|---|---|---|---|---|---|---|
| 31 | 53.5 | 1.5 | 353.61 (6) | − 12.9 (1) | 360.48 (6) | − 20.6 (1) | 11.4 | 0 | − 15 | 0 |
| 43 | 52.2 | 2.3 | 360.54 (6) | − 17.7 (1) | 355.53 (4) | − 12.7 (2) | 9.5 | − 15 | − 11 | 0.8 |
| 50 | 60.7 | 1.7 | 355.46 (4) | − 11.4 (2) | 362.50 (3) | − 19.5 (1) | 8.3 | − 11 | 0 | 0 |
| 62 | 56.9 | 1.9 | 362.52 (3) | − 19.5 (1) | 357.56 (5) | − 13.7 (1) | 6.3 | 0 | − 10 | 0.4 |
| 70 | 49.6 | 1.4 | 357.41 (6) | − 12.3 (1) | 364.52 (4) | − 19.1 (1) | 5.0 | − 10 | 0 | 0 |
| 33 | 54.1 | 2.2 | 356.55 (3) | − 19.3 (1) | 351.50 (3) | − 13.6 (2) | 14.0 | 0 | − 6 | 0 |
| 39 | 54.5 | 1.6 | 351.51 (3) | − 12.7 (2) | 358.65 (4) | − 20.9 (1) | 12.8 | − 6 | − 13 | 0.8 |
| 47 | 56.6 | 2.2 | 358.53 (4) | − 18.3 (1) | 353.51 (3) | − 12.7 (2) | 11.0 | − 13 | − 5 | 0.6 |
| 52 | 50.7 | 1.6 | 353.54 (3) | − 12.0 (2) | 360.45 (4) | − 18.8 (1) | 9.9 | − 5 | − 15 | 0.9 |
| 60 | 53.2 | 1.8 | 360.55 (4) | − 16.0 (1) | 355.57 (2) | − 11.5 (1) | 8.3 | − 15 | − 10 | 9 |
| 65 | 52.6 | 1.3 | 355.64 (2) | − 10.3 (1) | 362.57 (2) | − 16.3 (1) | 7.3 | − 10 | − 19 | 1.0 |
| 71 | 50.0 | 1.4 | 362.54 (3) | − 13.3 (1) | 357.44 (5) | − 9.7 (1) | 6.0 | − 19 | − 13 | 0.9 |
| 75 | 50.2 | 1.0 | 357.58 (5) | − 8.5 (1) | 364.49 (3) | − 13.1 (0) | 5.2 | − 13 | 0 | 0 |
| 30 | 47.2 | 2.1 | 345.53 (4) | − 9.2 (2) | 352.56 (4) | − 14.2 (1) | 19.1 | 0 | − 5 | 0 |
| 36 | 54.9 | 2.8 | 352.49 (3) | − 13.4 (1) | 347.58 (3) | − 9.4 (1) | 17.8 | − 5 | − 1 | 0.4 |
| 41 | 49.6 | 1.9 | 347.60 (3) | − 9.3 (1) | 354.58 (6) | − 14.5 (1) | 17.0 | − 1 | 0 | 0 |
| 51 | 50.0 | 2.3 | 349.51 (4) | − 9.1 (2) | 356.54 (6) | − 14.3 (1) | 14.9 | 0 | − 9 | 0 |
| 57 | 45.9 | 2.3 | 356.56 (6) | − 13.0 (1) | 351.43 (5) | − 9.6 (1) | 13.6 | − 9 | − 14 | 2.6 |
| 61 | 54.0 | 1.8 | 351.66 (5) | − 8.3 (1) | 358.63 (5) | − 13.4 (1) | 12.8 | − 14 | − 14 | 1.6 |
| 67 | 50.0 | 2.6 | 358.59 (5) | − 11.6 (1) | 353.57 (8) | − 8.4 (1) | 11.7 | − 14 | − 9 | 1.5 |
| 70 | 52.3 | 2.0 | 353.57 (8) | − 7.6 (1) | 360.51 (7) | − 12.1 (1) | 11.0 | − 9 | 0 | 0 |
| 72 | 51.9 | 1.3 | 368.42 (8) | − 10.6 (0) | 363.49 (5) | − 7.7 (0) | 7.5 | 0 | − 111 | 0 |
| 45 | 53.1 | 1.4 | 366.48 (7) | − 27.3 (1) | 361.54 (7) | − 19.7 (0) | 7.2 | 0 | − 23 | 0 |
| 57 | 51.5 | 0.9 | 361.58 (8) | − 15.5 (0) | 368.47 (7) | − 24.1 (1) | 5.6 | − 23 | − 31 | 0.8 |
| 72 | 68.6 | 1.7 | 368.50 (7) | − 17.5 (1) | 363.54 (6) | − 11.5 (1) | 3.7 | − 31 | − 30 | 1.0 |
| 78 | 53.0 | 1.0 | 363.43 (6) | − 8.5 (1) | 370.48 (5) | − 13.4 (0) | 2.8 | − 30 | 0 | 0 |
| 54 | 45.0 | 1.5 | 352.52 (4) | − 9.7 (1) | 359.63 (3) | − 14.5 (1) | 6.6 | 0 | − 17 | 0 |
| 62 | 51.9 | 1.4 | 359.54 (3) | − 12.2 (1) | 354.59 (2) | − 8.8 (1) | 5.4 | − 17 | 0 | 0 |

Headings as in Table 1.

**Table 4** Apparent activation energy data for PIBu degrading in vacuum

| DOC | *E* | Sig *E* | *T*1 | *R*1 | *T*2 | *R*2 | SWT (mg) | %*R*1 | %*R*2 | *n* |
|---|---|---|---|---|---|---|---|---|---|---|
| 53 | 72.7 | 2.5 | 314.55 (2) | – 5.0 (1) | 308.53 (2) | – 2.6 (0) | 9.9 | 0 | 0 | 0 |
| 87 | 52.4 | 1.7 | 342.51 (2) | – 2.1 (0) | 350.55 (2) | – 3.7 (0) | 2.7 | 0 | 0 | 0 |
| 75 | 63.4 | 1.2 | 315.56 (6) | – 2.9 (1) | 331.51 (4) | – 12.3 (1) | 8.0 | 0 | – 47 | 0 |
| 81 | 67.3 | 1.8 | 331.66 (4) | – 7.6 (1) | 338.71 (2) | – 14.4 (2) | 6.1 | – 47 | 0 | 0 |
| 89 | 51.2 | 1.8 | 333.61 (2) | – 3.4 (1) | 340.68 (2) | – 5.6 (0) | 3.3 | 0 | – 34 | 0 |
| 92 | 58.4 | 2.5 | 340.66 (2) | – 3.9 (0) | 335.64 (2) | – 2.6 (0) | 2.4 | – 34 | – 22 | 1.0 |
| 94 | 52.8 | 0.9 | 335.59 (2) | – 2.1 (0) | 351.53 (2) | – 6.4 (0) | 2.0 | – 22 | – 57 | 0.9 |
| 96 | 53.6 | 2.8 | 351.51 (2) | – 3.5 (0) | 346.45 (3) | – 2.5 (0) | 1.0 | – 57 | 0 | 0 |
| 79 | 62.6 | 1.7 | 332.69 (2) | – 2.2 (1) | 348.60 (2) | – 8.5 (1) | 4.3 | 0 | 0 | 0 |
| 87 | 49.8 | 1.5 | 343.61 (2) | – 2.2 (1) | 359.57 (2) | – 6.1 (1) | 2.5 | 0 | 0 | 0 |

Headings as in Table 1.

**Table 5** Average apparent activation energies for data given in Tables 1 through 4

| $N_2$ press., mm Hg | $E_u$ | $E_w$ | $\chi^2$ | $\hat{\sigma}$ | Percent data[a] removed | Procedure[b] |
|---|---|---|---|---|---|---|
| vacuum | 57 (2) | 56.7 (6) | 15 | 1.8 | 40 | TM |
| < 0.010 | 48 (2) | 57 (3) | 0.5 | 12 | 0 | PP |
| 99.995% | 52.2 (5) | 52.0 (3) | 1.1 | 1.7 | 30 | TM |
| 5 | 52.0 (5) | 51.9 (4) | 1.0 | 2.4 | 11 | PP |
| 99.995% | 49.2 (3) | 49.2 (1) | 2 | 0.7 | 29 | TM |
| 800 | 49.2 (3) | 49.2 (2) | 1 | 1.5 | 4 | PP |
| 99.95% | 48.6 (2) | 48.6 (1) | 2 | 0.7 | 20 | TM |
| 800 | 48.6 (2) | 48.6 (2) | 1 | 1.3 | 6 | PP |

The values in parentheses are the standard deviations in the least significant digit. $E_u$: winsorized value of unweighted average (trimmed values replaced by nearest unrejected value). $E_w$: average value calculated using weights of $1/\hat{\sigma}^2(E_i)$. $\chi^2$: value obtained for winsorized average of trimmed mean or from probability plot. *a*: arbitrarily set at 30 to 40 percent for trimmed mean estimate, corresponds to percentage rejected by probability plot program. The procedures are described in reference [11]. *b*: TM = trimmed mean estimate, PP = probability plot estimate. $\hat{\sigma}$: TM value: average of input values of sig $E$; PP value is average of sig $E$ values after scaling in probability plot procedure.

(238±12 kJ/mole). This is an average of those estimates of the activation energy obtained at greater than 40 percent degree of conversion and which passed the preaveraging scrutiny of rate of weight loss, $r > 2\,\mu v/s \sim 0.1\,\mu g/s$; $\sigma(r)/r < 4\%$, $\sigma(T) < 0.1^\circ$ where $T$ is the temperature, $\sigma(E) < 3$ kcal/mole; $E$ is the apparent activation energy and $\sigma$ is the estimated standard deviation.

The yield of monomer increases [8] in the range 300 to 400° as the temperature increases. With the exception of the activation energy cited in reference [4], the activation energy appears to be ~ 49 kcal/mole (200 kJ/mole) over a wide range of temperature (250° in reference [10], 306 to 326° in reference [13] and 365 to 405° here). Unzipping is thought to be the most significant degradation process. Transfer is considered to be a minor component of the degradation. The chain lengths are said to be at least 30 [4] and perhaps 100 [7], both much larger than the 10 steps or so required in the depolymerization step of the degradation mechanism to allow us to equate the overall activation energy, $E_a$, with the activation energies of initiation, $E_i$, depropagation, $E_d$, and biomolecular termination, $E_t$, in the form

$$E_a = \frac{E_i - E_t}{2} + E_d \tag{1}$$

A reasonable dissociation value for the C–C bond in PIBu is 78 kcal/mole (300 kJ/mole) which is the dissociation energy given by Benson [14] for the $(CH_3CH_2)–(tC_4H_8)$ bond. This bond dissociation energy is the difference in activation energies of the forward and back reactions, and is essentially the activation energy of the bond-breaking process, since the activation energy for radical-radical combination is 2±1 kcal/mole [15] (8±4 kJ/mole). The activation energy of the termination reaction is probably that of diffusion, which has been reported [16] to be 6.7 kcal/mole (28 kJ/mole) for long molecules in polyethylene and has been used in thermal degradation studies of polyethylene [17] and polypropylene [18]. Thus, substituting the above values of activation energy, we have

$$E_a = \frac{78 - 6.7}{2} + E_d \tag{2}$$

If the values of $E_a$ determined in $N_2$, i.e., 49.2 and 52.1 kcal/mole, are taken as representing the chemical degradation, then $E_d = 13.6$ to 15.5 kcal/mole (56.9 to 64.8 kJ/mole). However, if the $E_d$ is taken as the activation energy of the unzipping process, we may combine it with the heat of polymerization, $\Delta H_p$, of isobutylene to estimate the activation energy, $E_p$, of the reverse process, the addition of polyisobutyl radicals to the double bond in isobutylene, using the definition $\Delta H_p = E_p - E_d$. Values quoted for $\Delta H_p$ include $-$ 12.96±0.35 kcal/mole [19], $-$ 12.8 kcal/mole [20] and $-$ 17.20 kcal/mole [21]. The last value is not well documented, and therefore $\Delta H_p$ will be set equal to $-$ 13 kcal/mole (54 kJ/mole). Transformation of these values from 25° to 375°, a temperature typical of those used in the degradation studies reported here, involves a correction of 1 to 2 kcal/mole. Specific heats were taken from references [22] and [23]. With $\Delta H$ exothermic at $-$ 13 kcal/mole and $E_p \geqslant 0$, (because it is an activation energy) and $E_d = 13.6$ to 15.5 kcal/mole, the equation $E_p = \Delta H + E_d$ becomes

$$E_p = -13 + (13.6 \text{ to } 15.5) = 0.6 \text{ to } 2.5 \text{ kcal/mole.}$$

Because of the assumptions used in estimating $E_i$ and $E_t$ in equation (1), this value of $E_p$ is probably not significantly different from zero. This is similar to the value suggested in reference [15] for the combination of two radicals, but significantly different from the values of 6.9 to 7.3 kcal/mole given in reference [15] for addition of a range of alkyl radicals, from ethyl to t-butyl, to a double bond. For $E_p$ to be $\sim 7$ kcal/mole, $E_d$ would have to be $\sim 13.6 + 7 = 20$ kcal/mole, and the overall activation energy would have to be $\sim 49 + 7 = 56$ kcal/mole. This is essentially the value found for vacuum degradation here and will be taken as the activation energy representing the chemical degradation of PIBu, free from interference from physical effects. Other apparent overall activation energies have been found to be "too low" to represent the chemical steps in the degradation when the degradation was carried out in flowing $N_2$. This was the case for polyethylene [17] and polypropylene [18]. The difference was ascribed to contributions of the latent heat of vaporization in those cases [17, 18], where there is a significant amount of transfer and large molecules are formed and evaporated. (However, the same value was found for thermal degradation of polystyrene in vacuum and in $N_2$ [12], where the volatiles are monomer, with some dimer and trimer [24].) It appears that the activation energies for polyisobutylene degrading in vacuum and in N$_2$ are not the same. This is consistent with the mechanism containing a random scission step in addition to that of unzipping. Although the isobutylene molecules are extremely volatile under both inert atmospheres and vacuum conditions, the random scission component produces less volatile molecules, some of which undoubtedly evaporate significantly later than their formation.

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**Zusammenfassung** — Die gesamte Aktivierungsenergie der thermischen Zersetzung des Polyisobutylens wurde mittels der Factor-Jump-Thermogravimetrie gemessen, und in einem Bereich von 365 bis 405°C in N$_2$ mit einem Druck von 800 mm Hg, der mit einer Geschwindigkeit von 4 mm/s über die Probe strömte, für $49.2 \pm 0.3$ kcal/mol ($206 \pm 1$ kJ/mol) gefunden. Das stimmt mit einigen, für die thermische Zersetzung in Vakuum und in Lösung mitgeteilten Werten überein. Bei 5 mm Hg von N$_2$ wurde eine scheinbare Aktivierungsenergie von $52.1 \pm 0.5$ kcal/mol ($218 \pm 2$ kJ/mol), und in Vakuum die von $57 \pm 3$ kcal/mol ($238 \pm 13$ kJ/mol) gefunden. Ein störendes Brodeln erschwerte die Messung der Vakuumwerte. Die Substitution von annehmbaren Werten der anfänglichen Aktivierungsenergie $E_i$, des Endwertes $E_t$, und der Aktivierungsenergie $E_a$ für die Vakuumzersetzung in der Gleichung $E_a = E_i/2 + E_d - E_t/2$ gibt die Aktivierungsenergie $E_d = 84$ kJ/mol für die unzippinge Reaktion. Diese Gleichung setzt ein Zersetzungsmechanismus mit zufälliger Startreaktion, Unzipping und bimolekularem Ausgang voraus. Die Substitution von annehmbaren Werten der Polymerisationswärme $\Delta H$ in die Definition $\Delta H = E_p - E_d$ deutet darauf hin dass die Aktivierungsenergie der Polymerisationsreaktion bei 375°C ungefähr 7 kcal/mol (30 kJ mol) ist.

**Резюме** — Используя термогравиметрию с резким скачком температуры, была измерена суммарная энергия активации термического распада полиизобутилена, которая оказалась равной 49,2 ± 0,3 ккал/моль в области температур 365–405° в атмосфере азота при давлении 800 мм рт. ст. и при текучести газа над образцом 4 мм/сек. Это совпадает с некоторыми значениями, приведенными для термического распада в вакууме и в растворе. При давлении азота в 5 мм рт. ст. кажущаяся энергия активации была равной 52,1 ± 0,5 ккал/моль, а в вакууме — 57 ± 3 ккал/моль. Трудное барботирование делает трудным определение значения вакуума. Подставляя приемлемые значения энергий активации начальной реакции ($E_i$), конечной ($E_t$) и энергии активации $E_a$ при понижении вакуума в уравнение $E_a = E_i/2 + E_d - E_t/2$, получается значение энергии активации для немгновенной реакции равным $E_d = 20$ ккал/моль. Это уравнение включает в себя механизм распада произвольной начальной реакции, не мгновенной и бимолекулярной конечной реакции. Подставляя соответствующее значение теплоты полимеризации $\Delta H$ в уравнение $\Delta H = E_p - E_d$, получается, что значение энергии активации реакции полимеризации при 375° составляет приблизительно 7 ккал/моль.