[Contribution from Research and Development Laboratories, Celanese Chemical Company, Clarkwood, Texas]

Photolysis of Di-*t*-butyl Peroxide–Azomethane and Di-*t*-butyl Peroxide–Isobutane Mixtures

By G. R. McMillan

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These reactions have been studied by photolysis of mixtures of di-*t*-butyl peroxide with azomethane and with isobutane

$$(CH_3)_3CO \longrightarrow CH_3COCH_3 + CH_3 \quad (2)$$

$$(CH_3)_3CO + CH_3 \longrightarrow CH_3OC(CH_3)_3 \quad (5)$$

$$(CH_3)_3CO + (CH_3)_3CH \longrightarrow (CH_3)_3COH + (CH_3)_3C \quad (16)$$

An activation energy difference of 7 kcal. was found for $E_2 - E_{16}$. If reaction 5 has zero activation energy, E_2 is about 11 kcal. The ratio of disproportionation to recombination for methyl and *t*-butyl radicals was found to be 0.9 over the temperature range 25–79°.

Introduction

Several studies of the photochemical decomposition of di-*t*-butyl peroxide have appeared[1-4] and the main features of the reaction mechanism seem well understood. In the absence of a high concentration of a hydrogen donor, the *t*-butoxy radicals formed in the system disappear mainly by

$$(CH_3)_3CO \longrightarrow CH_3COCH_3 + CH_3 \quad (2)$$

Recent determinations of the activation energy of this reaction have yielded values of 11.2 ± 2[3] and 13.2 ± 2.4.[5] There is some experimental evidence that E_2 may be even lower.[4] Gray and Williams[6] accept 13 kcal. as the best value.

E_2 may be calculated from the temperature dependence of the rates of formation of acetone, ethane and methyl *t*-butyl ether. The ether is usually formed in trace quantities but its rate may be increased by decomposing mixtures of di-*t*-butyl peroxide and a photolytic methyl radical source. Azomethane was chosen because the long wave length ultraviolet absorption region of this compound does not seriously overlap that of the peroxide.[3,7]

The difference in activation energy between decomposition of the *t*-butoxy radical and abstraction of hydrogen from di-*t*-butyl peroxide in the vapor phase has been estimated to be 3 kcal.[4] Abstraction from isobutane, a molecule containing tertiary hydrogen, was studied for comparison.

Experimental

The di-*t*-butyl peroxide, a Shell Chemical Corp. sample, was distilled at reduced pressure and a center fraction stored at Dry Ice temperature on the vacuum line. The only impurities were a trace of water and a very small amount (<0.1%) of a compound presumed to be an octene from examination of its mass spectrum.

The azomethane was prepared from 1,2-dimethylhydrazine hydrochloride[8] by the method of Renaud and Leitch.[9] The crude product was fractionally distilled, dried over Drierite in the vacuum line and stored in a blackened bulb. Most samples prepared for photolysis contained about 1% methyl chloride. Some samples contained as much as 3% of this impurity.

The isobutane was Phillips Research Grade.

Two mercury arcs were used: a Hanovia S-500 lamp and a General Electric B-H6 air cooled arc. No filters were employed.

The apparatus was a conventional vacuum system consisting of reaction cell, traps, Ward still and Toepler pump-gas buret. The electrically heated quartz reaction vessel was isolated by a mercury float valve. A mixing bulb was connected at the outlet of the cell. Samples could be condensed directly from the analytical section of the vacuum line into the inlet of the gas chromatograph.

The reactants were carefully degassed, introduced separately into the cell and mixed by expanding several times into the mixing bulb before start of the photolysis. After irradiation was stopped, a fraction of products not condensed at −160° was removed, measured in the gas buret and transferred to a mass spectrometer tube. Condensable products and excess reactants were separated by gas chromatography on di-2-ethylhexyl sebacate-Celite. Components were trapped as they left the column and analyzed with the mass spectrometer.

In the experiments with azomethane-di-*t*-butyl peroxide mixtures, the amounts of acetone formed were computed from the area under the chromatographic peak; in the experiments with isobutane-di-*t*-butyl peroxide mixtures, the observed rate of acetone production was computed from the methyl balance

$$R_{CH_3COCH_3} = 2R_{C_2H_6} + R_{CH_4} + R_{C_5H_{12}} - 2R_{CO}{}^4$$

In both cases the true rate of acetone formation, which is given in the tables, was obtained by adding the observed rate to the rate of carbon monoxide formation. Rates of the other "liquid" products were calculated from the observed rate of acetone and the mass spectrometrically determined product ratios.

Isobutylene and neopentane rates were calculated by mass spectrometric analysis of the chromatographic fraction which contained in addition isobutane and sometimes some ethane. Since isobutane usually constituted 99% of this fraction, the rates of isobutylene and neopentane may be somewhat in error.

Propane amounted to about 1% of the ethane in experiments with azomethane and di-*t*-butyl peroxide. This was considered to be formed by secondary reactions of ethane and was computed as such.

Results

(a) Azomethane–Di-*t*-butyl Peroxide Mixtures.—The fraction of products volatile at −160° contained ethane, nitrogen, methane and some propane and carbon monoxide. The liquid products identified were acetone, methyl *t*-butyl ether, *t*-butyl alcohol and isobutylene oxide. No study of the other liquid products was made but small contributions to *m/e* peaks 71 and 72 in the product spectra suggest methyl ethyl diimide.

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[1] E. R. Bell, F. F. Rust and W. E. Vaughan, This Journal, **72**, 337 (1950).

[2] L. M. Dorfman and Z. W. Salsburg, *ibid.*, **73**, 255 (1951).

[3] D. H. Volman and W. M. Graven, *ibid.*, **75**, 3111 (1953).

[4] G. McMillan and M. H. J. Wijnen, *Can. J. Chem.*, **36**, 1227 (1958). The sequence of reaction numbering in this reference is maintained in the present paper.

[5] F. W. Birss, C. J. Danby and C. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A239**, 154 (1957).

[6] P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

[7] H. C. Ramsperger, This Journal, **50**, 123 (1928).

[8] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 208.

[9] R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

TABLE I

PHOTOLYSIS OF DI-*t*-BUTYL PEROXIDE–AZOMETHANE MIXTURES

Pressure of di-*t*-butylperoxide, 20 mm.; rates in molecules/ml./sec. × 10^{-12}

Temp., °C.	10^{-17} $[(CH_3)_2N_2]i$, molecules/ml.	Time, sec.	Lamp[a]	$R_{CH_3COCH_3}$	$R_{CH_3OC(CH_3)_3}$	$R_{C_2H_6}$	R_{N_2}	R_{CH_4}	R_{CO}	10^{-8} $k_2k_8^{1/2}/k_5$ (molecule/ml./sec.)$^{1/2}$
24	8	1800	S	33.52	0.46	39.85	31.63	1.39	0.51	4.60
24	10	1800	S	40.48	.55	48.07	39.85	1.83	.57	5.10
25	9	1920	S	10.67	.11	25.50	21.35	0.89	.47	4.90
25	14	1800	S	9.49	.11	20.24	18.34	0.88	.19	3.88
27	8	1800	S	29.73	.30	41.75	32.26	1.33	.44	6.40
29	12	1800	S	17.71	.18	46.17	41.75	1.83	.82	6.69
30.5	13	1020	B	20.09	.48	137.3	139.5	2.01	1.45	4.91
32	13	900	B	29.10	.48	130.3	132.8	2.40	2.40	6.92
33	12	1800	S	16.44	.12	30.99	24.67	1.20	0.38	7.63
35	12	1800	S	15.18	.08	44.91	36.69	1.77	0.82	12.7
37	11	900	B	29.10	.44	131.6	127.8	2.15	1.01	7.59
38	6	900	B	36.69	.40	77.17	64.52	1.14	1.01	8.06
39	13	1800	S	18.34	.10	44.90	41.75	2.02	0.44	12.3
44	5	1800	S	24.67	.10	34.79	24.04	1.39	.70	14.6
44	12	900	B	18.98	.18	112.6	113.9	2.28	.63	11.2
45	12	900	B	26.57	.22	97.40	86.02	1.90	.50	11.9
45	18	900	B	22.77	.19	182.2	207.5	4.80	2.02	16.2
51	15	900	B	36.69	.22	183.4	178.4	4.05	2.53	22.6
51	18	900	B	39.85	.23	186.0	210.0	7.45	7.45	23.6
51	20	900	B	37.95	.28	208.7	234.0	5.44	2.28	19.6
51	26	900	B	35.42	.23	259.3	298.5	7.96	3.41	24.8
52	17	900	B	37.95	.23	184.7	206.2	5.18	2.40	22.4

[a] S = Hanovia S-500; B = General Electric B-H6 Lamp.

The results at several temperatures and azomethane concentrations are shown in Table I. An examination of the methyl radical balance shows $R_{CH_3COCH_3} + 2R_{N_2} > 2R_{C_2H_6} + R_{CH_4}$. This is interpreted as evidence for formation of compounds such as tetramethylhydrazine and methyl ethyl diimide.

(b) **Isobutane–di-*t*-butyl Peroxide Mixtures.**—The fraction volatile at −160° contained ethane, methane and carbon monoxide. Condensable products included acetone, *t*-butyl alcohol, isobutylene oxide, isobutylene, neopentane and sometimes traces of methyl *t*-butyl ether. No traces could be found of di-*t*-butyl ether, 2,2,3,3-tetramethylbutane, methyl *t*-butyl ketone and 2-methylbutane. Results of experiments at different temperatures and isobutane concentrations are given in Table II.

Discussion

The mechanisms accounting for most of the experimental facts in the photolysis of di-*t*-butyl peroxide vapor at temperatures below 80°[4] are

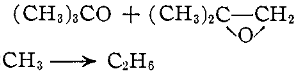
$$(CH_3)_3COOC(CH_3)_3 + h\nu \longrightarrow 2(CH_3)_3CO \quad (1)$$

$$(CH_3)_3CO \longrightarrow CH_3COCH_3 + CH_3 \quad (2)$$

$$CH_3 + (CH_3)_3CO \longrightarrow CH_3OC(CH_3)_3 \quad (5)$$

$$(CH_3)_3CO + (CH_3)_3COOC(CH_3)_3 \longrightarrow (CH_3)_3COOC(CH_3)_2CH_2 + (CH_3)_3COH \quad (6)$$

$$(CH_3)_3COOC(CH_3)_2CH_2 \longrightarrow$$



$$(CH_3)_3CO + (CH_3)_2C\underset{\diagdown O \diagup}{\text{—}}CH_2 \quad (7)$$

$$2CH_3 \longrightarrow C_2H_6 \quad (8)$$

$$CH_3 + (CH_3)_3COOC(CH_3)_3 \longrightarrow CH_4 + (CH_3)_3COOC(CH_3)_2CH_2 \quad (9)$$

$$CH_3COCH_3 + h\nu \longrightarrow CH_3 + CH_3CO \quad (10)$$

$$CH_3 + CH_3CO \longrightarrow CH_3COCH_3 \quad (11)$$

$$CH_3CO \longrightarrow CH_3 + CO \quad (13)$$

Reaction 5 is relatively unimportant. The following reaction, among others, must be added when mixtures of di-*t*-butyl peroxide with azomethane are photolyzed.

$$CH_3NNCH_3 + h\nu \longrightarrow 2CH_3 + N_2$$

The usual treatment of mechanism gives

$$R_{CH_3COCH_3} \times R^{1/2}_{C_2H_6}/R_{CH_3OC(CH_3)_3} = k_2k_8^{1/2}/k_5 \quad A$$

The rate constant ratios obtained from experiments on azomethane–di-*t*-butyl peroxide mixtures are given in Table I and the Arrhenius plot in Fig. 1. The least squares activation energy $E_2 - E_5 + {}^1/_2 E_8$ is 11 kcal. If E_5 and E_8 are taken to be zero, this value may be associated with E_2. The value probably is correct to ± 2 kcal. This agrees very well with 11.2 ± 2 kcal. obtained by Volman and Graven from their study of the *t*-butoxy initiated polymerization of butadiene.[3] From the results of Shepp,[10] k_8 is about 3.65 × 10^{-11} ml./molecule/sec.[10]; k_5 is probably about the same. Combining these constants with the present data gives $k_2 \cong 10^4$ sec.$^{-1}$ at 51°. If E_2 is 11 kcal., $A_2 \cong 10^{11}$ sec.$^{-1}$, which lies in the lower part of the range expected for a unimolecular reaction.

When di-*t*-butyl peroxide is decomposed in the presence of isobutane, the reactions which must be added are

$$(CH_3)_3CO + (CH_3)_3CH \longrightarrow (CH_3)_3COH + (CH_3)_3C \quad (16)$$

$$CH_3 + (CH_3)_3CH \longrightarrow CH_4 + (CH_3)_3C \quad (17)$$

$$CH_3 + (CH_3)_3C \longrightarrow CH_4 + (CH_3)_2C{=}CH_2 \quad (18)$$

$$\longrightarrow (CH_3)_4C \quad (19)$$

If any isobutyl radicals were formed in this system, some 2-methylbutane should be formed

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[10] A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956).

Table II

Photolysis of Di-*t*-Butyl Peroxide–Isobutane Mixtures

Concentration of di-*t*-butyl peroxide, 5.85 ± 0.05 × 10^{17} molecules/ml.; reaction time, 1800 sec.; rates in molecules/ml./sec. × 10^{-12}

10^{-17} $[i\text{-}C_4H_{10}]t$, molecules/ml.	$R_{CH_3COCH_3}$	$R_{C_2H_6}$	R_{CH_4}	R_{CO}	$R_{(CH_3)_3COH}$	$R_{i\text{-}C_4H_8}$	$R_{neo\text{-}C_5H_{12}}$	$R_{(CH_3)_2C\underset{O}{\diagdown\diagup}CH_2}$
				$T = 25°$				
0	34.16	17.58	0.95	1.20	1.90	..	..	0.51
11.66	34.16	14.10	2.34	0.63	6.07	3.1	3.7	.38
18.47	29.10	12.08	2.78	.76	7.27	3.0	3.0	.19
23.65	30.36	12.27	2.66	.70	8.03	5.1	3.8	.51
33.05	30.36	10.50	3.16	.70	10.63	5.3	7.1	.13
				$T = 36°$				
0	31.63	15.81	0.76	0.89	1.64	..	..	0.51
0	32.89	16.38	0.76	.76	1.52	..	..	.51
11.23	27.20	12.27	1.77	.76	3.35	1.8	1.8	.25
16.22	27.20	11.95	2.02	.70	4.55	1.8	1.8	.38
22.46	24.04	8.16	2.34	.70	4.30	2.4	3.6	.13
30.58	25.93	8.54	5.95	.63	5.88	3.3	3.3	.25
				$T = 55°$				
0	42.38	21.39	1.08	1.27	1.01	..	..	0.38
0	42.38	21.25	1.20	1.33	0.95	..	..	.44
0	44.91	26.48	1.20	0.89	1.14	..	..	.50
6.62	43.01	20.05	1.96	1.14	2.34	1.8	2.2	.25
12.05	34.79	15.56	2.09	1.27	2.43	2.0	2.6	.19
14.55	37.95	17.08	2.91	1.52	1.86	1.6	2.3	.19
16.17	40.48	18.41	2.59	1.52	2.92	3.5	2.6	.19
19.70	43.01	18.47	2.78	1.64	4.49	2.1	3.2	.25
22.92	52.50	22.83	3.86	1.45	3.85	3.2	8.2	.95
24.69	45.54	18.72	4.05	1.39	8.15	4.0	5.3	.38
28.81	43.64	18.84	3.16	1.14	4.74	3.1	3.1	.32
				$T = 79°$				
0	34.16	17.33	1.39	3.15	0.57	..	..	0.44
0	37.32	18.84	0.89	1.39	0.69	..	..	.57
0	39.85	20.18	1.07	1.90	1.08	..	..	.57
5.75	46.17	22.14	2.34	2.34	1.14	1.5	1.8	.12
13.97	38.58	17.77	2.47	1.45	1.33	2.3	2.3	.19
20.55	34.16	14.86	4.24	1.77	1.52	2.2	2.2	.06
27.95	25.93	9.67	4.55	1.52	1.14	1.3	3.0	.06
28.50	34.16	13.79	5.25	1.58	1.39	3.0	3.0	.06
29.04	37.95	15.69	5.06	1.45	1.77	3.1	3.1	.12

by recombination of isobutyl and methyl radicals. Failure to find 2-methylbutane in the products indicates predomination of tertiary hydrogen abstraction.

The mechanism yields

$$R_{(CH_3)_3COH}/R_{CH_3COCH_3} = k_6/k_2[\text{DTBP}] + k_{16}/k_2[i\text{-}C_4H_{10}] \quad B$$

The ratios of *t*-butyl alcohol to acetone are plotted in Fig. 2 for different temperatures and isobutane concentrations at constant di-*t*-butyl peroxide concentration. The ratios of rate constants k_{16}/k_2 found are: 25°, 9.4; 36°, 5.9; 55°, 3.2; 79°, 1.4, all × 10^{-20} in units of ml./molecule.

The values of k_{16}/k_2 will be in error if any *t*-butyl alcohol is formed by disproportionations such as

$$(CH_3)_3CO + (CH_3)_3C \longrightarrow (CH_3)_2C{=}CH_2 + (CH_3)_3COH \quad (20)$$

From consideration of the rates of product formation, *t*-butyl and *t*-butoxy radicals are never in high concentration and (20) is not considered important in this system except possibly at the lowest temperature. Furthermore, no trace of the recombination product of *t*-butyl and *t*-butoxy could be detected.

The balance for *t*-butyl radicals requires $R_{(CH_3)_3COH} + R_{CH_4} > 2R_{C_4H_8} + R_{C_5H_{12}}$. This inequality is not observed, due probably to errors in measurement of isobutylene and neopentane.

The ratios of the rate constants for disproportionation and recombination of methyl and *t*-butyl radicals may be calculated from the equation

$$R_{i\text{-}C_4H_8}/R_{neo\text{-}C_5H_{12}} = k_{18}/k_{19}$$

The mean values are: 25°, 0.98; 36°, 0.92; 55°, 0.81; 79°, 0.88. There is considerable scatter at all temperatures; it therefore seems preferable to average all the ratios observed and report k_{18}/k_{19} = 0.9 (0.88) over the temperature range 25–79°.

The Arrhenius plot of k_{16}/k_2 (Fig. 3) yields a value of $E_2 - E_{16}$ of 7 kcal. This difference is consistent with values of 7–8 kcal. reported by Brook[11] for $E_2 - E_{\text{abstraction}}$ in liquid phase experiments with hydrocarbons containing tertiary hydrogen atoms. If E_2 is 11 kcal., E_{16} is 4 kcal. The value of k_2 at

[11] J. H. T. Brook, *Trans. Faraday Soc.*, **53**, 327 (1957).

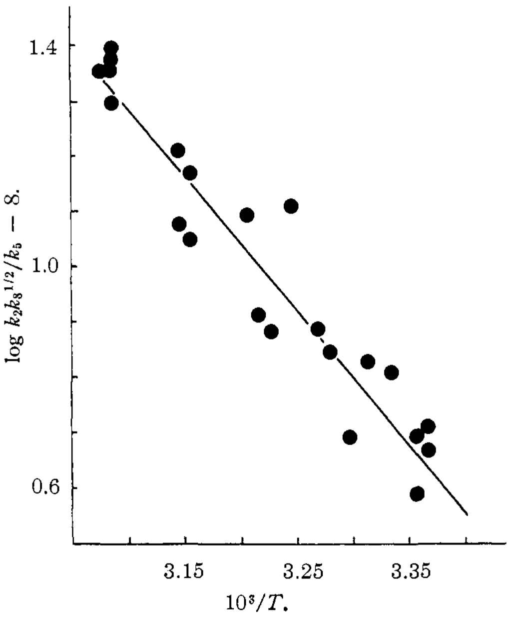

Fig. 1.—Arrhenius plot of $k_2k_8^{1/2}/k_5$.

51° based on an assumed rate constant for the recombination of methyl and *t*-butoxy radicals was shown above to be about 10^4 sec.$^{-1}$. From the value obtained for k_{16}/k_2 at 51°, A_{16} can be calculated to be the order of 10^{-13} ml./molecule/sec., that is, in line with the A factors observed for abstraction reactions of methyl radicals.

Since $E_2 - E_6$ has been shown to be 3 kcal., $E_6 - E_{16}$ is 4 kcal. This difference in activation energy for abstraction of primary and tertiary hydrogen is consistent with considerable selectivity in the abstraction reactions of *t*-butoxy radicals.

Wijnen has established an activation energy of 4.5–5 kcal. for abstraction of hydrogen from methyl acetate by methoxy radicals.[12] If E_2 is 11 kcal., E_{16} is 4 kcal. This would indicate that the methoxy radical abstracts primary hydrogen with an activation energy comparable with that required for abstraction of a tertiary hydrogen by the *t*-butoxy radical. The *t*-butoxy radical may thus be somewhat less reactive in abstraction than the methoxy radical. This would not be expected from consideration of bond dissociation energies, since according to the compilation of Gray and Williams,[4] $D_{t\text{-C}_4\text{H}_9\text{O-H}}$ is greater by 4 kcal. than $D_{\text{CH}_3\text{O-H}}$.

E_2 must still be considered uncertain by a few kcal. More work also needs to be done on the possibility of E_2 being affected in photolytic systems by hot radical effects.

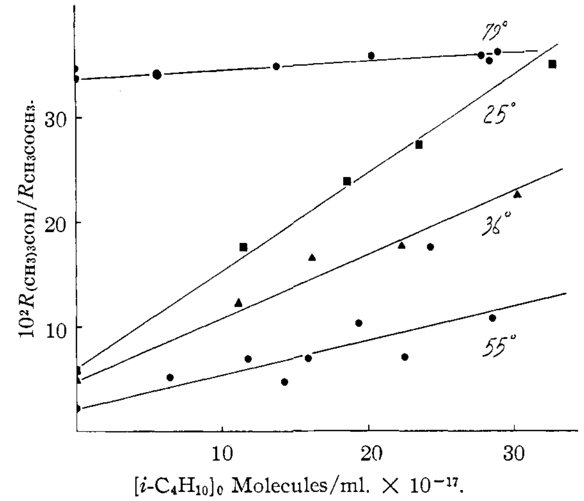

Fig. 2.—Dependence of $R_{(\text{CH}_3)_3\text{COH}}/R_{\text{CH}_3\text{COCH}_3}$ upon concentration of isobutane at various temperatures. Data at 79° scaled +32 units along ordinate scale.

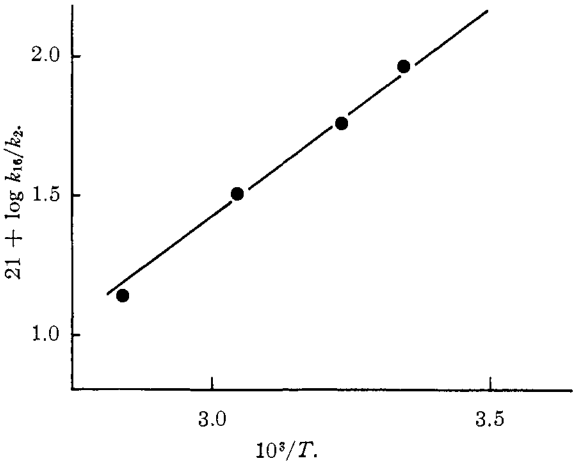

Fig. 3.—Arrhenius plot of k_{16}/k_2.

NOTE ADDED IN PROOF: Frey [*Proc. Chem. Soc.*, 385 (1959)] has shown that a second primary process, due to low wave length radiation, produces *t*-butyl radicals and possibly oxygen. Under the conditions of the present experiments, this reaction amounts to not more than about 1% of the total primary decomposition. In experiments carried out in this laboratory on diisopropyl peroxide, the process producing isopropyl radicals has been found to occur in the photolysis with unfiltered light, but not when the radiation is restricted to the region $\lambda > 2300$ Å. Thus, the importance of the process reported by Frey will depend upon the quality and thickness of the quartz window of the reaction cell as well as the wave length distribution of the lamp output.

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[12] M. H. J. Wijnen, *J. Chem. Phys.*, **27**, 710 (1957); **28**, 939 (1958).