Glossary

$A(T)$	empirical linear function of absolute temperature
$B(T)$	empirical linear function of absolute temperature
$C(T)$	empirical linear function of absolute temperature
$D(T)$	empirical linear function of absolute temperature
$F(T,N_{COO})$	empirical function of the absolute temperature and the number of carboxyl groups.
$I'(T)$	empirical linear function of absolute temperature
K	$[C(T)N_2 + D(T)]/F(T,N_{COO})$, coefficient of λ^2
λ	$[B(T)N_{COO} + A(T)]/M$
M	molecular weight
N_2	number of methylene groups per molecule
N_{COO}	number of carboxyl groups per molecule
$(N_{COO}/M)_0$	ratio of number of carboxyl groups of the repeating unit to the molecular weight of the unit
ρ	density, g/cm^3
ρ_∞	density at infinite chain length, g/cm^3
T	absolute temperature, K

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Vapor Pressure of Di-tert-butyl Peroxide

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The vapor pressure of di-tert-butyl peroxide was determined and a predictive equation for its calculation is given. The molar heat of vaporization was calculated as 7.63 kcal.

Di-tert-butyl peroxide is quite useful as a source of free radicals in kinetic studies (2) and in high-temperature polymerizations (5). Di-tert-butyl peroxide, unlike the lower alkyl peroxides such as dimethyl, methyl ethyl, and diethyl, is rather stable to both heat and shock. It will decompose oxidatively and thermally at elevated temperatures but not with the severity associated with the lower alkyl peroxides. A cool flame, the emission of $^1A_2$ H_2CO, from the oxidative decomposition of di-tert-butyl peroxide has been observed at approximately 550 K (6). At room temperature di-tert-butyl peroxide is quite stable and safe to handle (3). Dimethyl peroxide, however, is extremely shock sensitive and must be handled with utmost care.

In using di-tert-butyl peroxide as a radical source, it can be delivered by passing an inert gas stream through the liquid peroxide. The vapor concentration of peroxide is dictated by its vapor pressure. Therefore, the vapor pressure was measured and fitted to the integrated Clausius–Clapeyron equation. A value for the molar heat of vaporization of the peroxide was also calculated.

Experimental Section

The di-tert-butyl peroxide obtained from Matheson Coleman and Bell (Stock no. BX2020) was assayed by MCB at 99.7% purity with GC and IR spectra.

Table I. Vapor Pressure of Di-tert-Butyl Peroxide

Temp, °C	Pressure, Torr	Temp, °C	Pressure, Torr
−26.5	1.806	−4.0	7.695
−23.0	2.351	−3.0	7.709
−22.0	2.952	−3.0	8.660
−22.0	2.950	2.0	10.040
−22.0	2.825	4.0	11.324
−22.0	2.657	6.0	12.40
−22.0	2.459	10.0	15.08
−21.0	2.612	10.0	15.54
−20.5	2.925	14.0	19.08
−18.0	3.603	14.0	18.90
−17.5	3.491	16.0	20.29
−16.0	4.037	17.0	22.11
−16.0	3.933	20.0	27.24
−14.0	4.003	20.0	24.73
−12.0	5.371	24.0	30.40
−12.0	5.065	24.0	28.84
−10.0	5.350	25.0	31.34
−9.0	5.517	30.0	38.67
−7.0	7.192	31.0	39.65
−5.5	7.306	31.5	38.88
−5.0	7.936	33.0	39.16
−4.0	8.319	38.0	49.94
−4.0	7.740	40.0	48.14

Standard vapor pressure measurements were made by allowing an excess of liquid to equilibrate in an enclosed system resting in a Haake Model FK constant-temperature bath. Integral to the enclosed system was an MKS Model 144 Baratron for pressure measurements ($\pm$0.001 Torr for less than 11.500 Torr
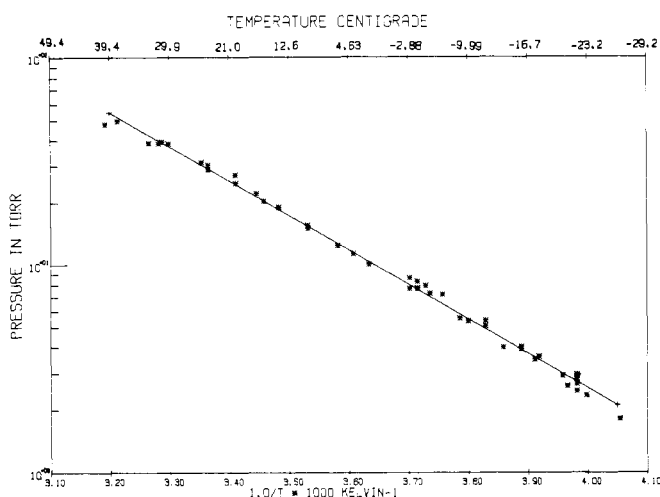
Figure 1. Vapor pressure of di-*tert*-butyl peroxide: (*) experimental points, (+) calculated least-squares best fit line with $r^2 = 0.996$.

Clausius–Clapeyron equation (*1*) relates vapor pressure to temperature

$$\ln P = (-\Delta H_v/R)(1/T) + \text{constant} \qquad (1)$$

where P is the pressure, T the temperature in Kelvin, R the universal gas constant, and ΔH_v the molar heat of vaporization. The value of the constant depends in part on the units used for the pressure. The experimental values were fitted to eq 1 using the method of least squares. The best fit line is

$$\ln P = (-3.842 \times 10^3)(1/T) + 1.630 \times 10^1 \qquad (2)$$

where P is in Torr. Equation 2 or the vapor pressure curve in Figure 1 can be used to obtain vapor pressures to assist in the design of experiments. The coefficient of determination for the calculated line is 0.996. The calculated molar heat of vaporization is 7.63 kcal.

and ±0.01 Torr for greater than 11.500 Torr). Temperature was measured with a chromel–alumel thermocouple resting in the liquid of the constant-temperature bath. The thermocouple was attached to a strip chart recorder and the pressure measurement was taken approximately 15 min after there was no detectable temperature change.

Results

The vapor pressure data are shown in Table I. The integrated

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Pressure–Temperature Relationship for Decomposition of Sodium Bicarbonate from 200 to 600 °F

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The equilibrium dissociation pressure of initially dry sodium bicarbonate (nahcolite) was experimentally determined between 200 and 600 °F. It was found necessary to use a constant ratio of initial gas volume to solid nahcolite volume, V_g/V_s, to obtain a unique pressure–temperature curve. Such pressure–temperature relationships were measured for three values of V_g/V_s, each curve showing three points of discontinuous slope. For $V_g/V_s = 1$, the pressure exceeded 6000 psia above 487 °F. Since the Green River oil shale formation in Colorado contains both beds and isolated nodules of nahcolite, the pressure developed by heating nahcolite may be a factor in developing porosity and permeability during an in situ thermal process for producing shale oil.

The Green River oil shale formation in the Piceance Basin, Colo., contains both layers and isolated nodules of nearly pure nahcolite (sodium bicarbonate) at depths between 1500 and 2300 ft. The dissolving of the layered nahcolite with warm water is a feature of planned in situ shale oil recovery processes de-

signed to create initial porosity. As a cavity wall is heated in the leaching and rubbling phase of the process, sealed-off nahcolite nodules will be heated and will develop a dissociation pressure due to the tendency to evolve carbon dioxide and water vapor. At high enough temperatures this pressure should become large enough to cause the nodules to "pop", thus causing cracking or rubbling of the cavity wall. This overall phenomenon could then be a mechanism for cavity growth.

The most complete set of decomposition pressures and temperatures of sodium bicarbonate available appears to be that of Caven and Sand (*2*) who made measurements between 86 and 230 °F. Within this temperature range the molar amounts of water and carbon dioxide evolved were equal; thus the decomposition under these conditions is represented by the reaction

$$2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g) \qquad (1)$$

nahcolite   soda ash
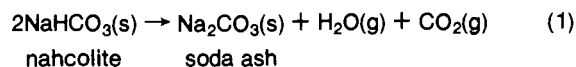
Thus no water condensed or formed solid hydrates. They reported their smoothed data as the equation