Table I. System Naphthalene-Ethylbenzene at 25° C.

x_2, Mole Fraction Naphthalene	V°, Ml. per Mole	
	Exptl.	Calcd.
0	122.83	122.83
0.0420	122.87	122.88
0.0840	122.91	122.92
0.1250	122.98	122.98
0.1723	123.05	123.04

of a plot of V° vs. x_2. This was done by the method of least squares, forcing the regression line to pass through $V^\circ = V^\circ_1$ at $x_2 = 0$. This requirement was imposed on the principle that density determination on the pure solvent involved fewer sources of error.

A value of 123.98 ml. per mole was found for V°_2. For the four mixtures, the experimental and calculated values of V° are compared in Table I. The agreement is within experimental error for all mixtures.

The experimental value of V°_1, 122.83 ml. per mole, differs from the literature value of 123.06 (1) by about 0.2%. Both this and the refractive index indicate a measurable

impurity in the solvent. Previous work (2) has shown, however, that the effect thereof should be negligible.

When the interaction between mixture components is sufficiently small, Henry's law behavior at low solute concentrations coincides experimentally with Raoult's law behavior. The upper limit of concentration observed here is about 0.2 mole fraction of naphthalene, which extends beyond the usual limit of the Henry's law region. As the volumetric data at the high concentration agree with those at the lower concentration, this is taken to indicate that V°_2 reported here does represent the molar volume of pure supercooled naphthalene, rather than an apparent molar volume.

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# Heat of Reaction and Dissociation Energy for the C—C Bond in 1,2-Dimethoxy-1,1,2,2-tetraphenyl Ethane

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The dissociation energy for the $\phi_2(OCH_3)C$—$C(OCH)\phi_2$ bond, as determined by ESR, is 30.0 $\pm$ 0.6 kcal. per mole. The activation energy for the recombination of α-methoxydiphenylmethyl radicals is approximately zero.

CONTINUING their interest in the physical properties of the α-methoxydiphenylmethyl radical (3), the authors have measured the equilibrium constant of the

$$R—R \;=\; 2R \cdot$$
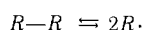
reaction over the temperature range of 77° to 120° C. by measuring the radical concentration with ESR.
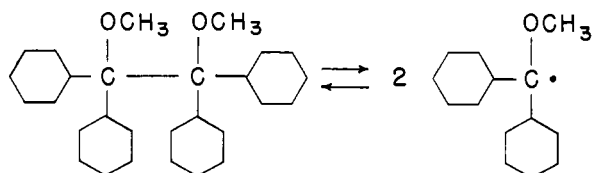
Below 77° C. the signal-to-noise ratio is low, and at 120° C. the steady state radical concentration decays by means of side reactions, with a half-life of 25 minutes.

At intermediate temperatures, the system is sufficiently stable to permit reliable equilibrium measurements. The change in radical concentration follows the temperature change so closely that no activation energy can be observed for the recombination of radicals, as is the case with the trityl radical(2). Therefore, the heat of reaction is assumed to be the dissociation energy of the $\phi_2(OCH_3)C$—$C(OCH_3)\phi_2$ bond.

The calculated data in Table I were obtained from a least squares fit to the equation

$$K_{eq} = \exp\left[\frac{(-15109 \pm 303)}{T} + 17.93 \pm 0.82 \right]$$

from which

$$\Delta H = D[\phi_2(OCH_3)C—C(OCH_3)\phi_2] = R \times \frac{d(\ln K_{eq})}{d(1/T)} =$$

$$30.0 \pm 0.6 \text{ kcal. per mole}$$

The substitution of methoxy groups for phenyl in trityl increases the C—C bond strength by 12 kcal. per mole, which is substantially the same as suggested by Conant (1) when a phenyl group is replaced by hydrogen.

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Table I. Equilibrium Constants

$K_{eq} \times 10^{11}$	Calcd. $K_{eq} \times 10^{11}$	Temp., °K.	Radical Concn. $\times 10^6$ Moles/Liter
1.25	1.16	350.5	1.04
4.23	4.33	361.5	1.91
12.4	14.1	372.0	3.28
40.6	40.8	382.0	5.92
123.0	114.0	392.5	10.3

EXPERIMENTAL

A solution of 0.102 gram per 3.0 ml. of toluene was sealed in a 3-mm. i.d., 4-mm. o.d. tube (Pyrex 7740) after several freeze-thaw cycles under vacuum.

The electron spin resonance spectra were obtained using a Varian V4500-10A spectrometer with a V4540 temperature controller. The temperature was determined by measuring the e.m.f. of a copper-constantan thermocouple with a Leeds and Northrup Model 8691 potentiometer. The concentra-tion was determined by comparison with a diphenylpicryl-hydrazyl solution, which was measured optically with a Cary Model 15 recording spectrophotometer, using a molar extinction coefficient of 13,300 at 530 mμ (4).

The calculations were made with the assistance of a time-sharing Burroughs B-5500 computer.

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