Equilibrium Dissociation of Triphenylmethyl Dimer

By Karla S. Colle, P. Scott Glaspie, and Edward S. Lewis*
(*Department of Chemistry, Rice University, Houston, Texas* 77001)

Summary New spectrophotometric measurements of the degree of dissociation of trityl dimer are in agreement with those obtained previously; the discrepancies of the magnetic susceptibility method disappear when the correct dimer structure is used in the diamagnetic correction.

The extent of dissociation of the dimer of the trityl radical is important to the understanding of organic free radicals. Several measurements have been made, but only two are quantitatively convincing; the spectrophotometric measurements based on Beer's law deviation by Ziegler,[1] and the measurement of magnetic susceptibility by Müller,[2] later extended by Selwood[3] and Marvel.[4]

Unfortunately, the two measurements are not in quantitative agreement; a discrepancy of about a factor of two was noted by Wheland.[5] An error found in the spectrophotometric measurements, when applied to many *p*-alkyl substituted trityl radicals,[6] has led to the neglect of this approach.

We have now repeated the spectrophotometric measurements closely following Ziegler, but using a modern spectrophotometer and a better method for placing known solutions in the spectrophotometer without exposure to air. In toluene, $K = \exp[(-47{\cdot}03\text{ kJ} + 0{\cdot}09434T)/RT]$. The various results are shown in the Table. The magnetic method requires knowledge of the diamagnetic susceptibility of the free radical and its dimer, both originally calculated using Pascal's constants. However, the free radical is delocalized so that the diamagnetic term may be too small. We attempted to estimate this correction using Selwood and Dobres'[7] measurements on the tris-*p*-t-butyl-

Temp/°C	Solvent	$K \times 10^4$/M Spectrophotometric	$K \times 10^4$/M Magnetic	$K \times 10^4$/M Corrected dimer structure	$K \times 10^4$/M Corrected dimer and monomer exaltation
0°	Toluene	0·791,[a] 0·758[b]			
10°	Toluene	1·47,[a] 1·57[b]			
20°	Toluene	3·08,[a] 3·12[b]			
23°	Benzene	4·11[c]	2·3[d]	4·14	3·9
30°	Toluene	5·91,[a] 5·90[b]	2·89[e]	9·5	10·25
			3·13[e]	10·48	11·3
40°	Toluene	10·72[b]	3·64[e]	11·65	12·6
50°	Toluene	18·75[b]	7·3[e]	24·75	26·9
			6·96[e]	23·0	25·2
60°	Toluene	31·73[b]	11·5[e]	37·9	41·4

[a] This work. [b] This work, calculated values from temperature dependence in text. [c] Ref. 1. [d] Ref. 2. [e] Ref. 3.

phenylmethyl radical. They calculated 70% dissociation, but it was not temperature sensitive, suggesting 100% dissociation. This error, as they suggested, could arise from a wrong diamagnetic susceptibility calculation.

We support Selwood's suggestion that tris-*p*-t-butyphenylmethyl radical does not dimerize. A solution of the radical in toluene is unaltered in colour after being held for weeks at −78°, suggesting that no important equilibrium dimerization of the radical occurs, even at this low temperature.

The failure to dimerize is also consistent with the recently demonstrated structure of the dimer of triphenylmethyl,[8] since the *p*-t-butyl group could cause significant steric hindrance. The calculation backwards of the monomer susceptibility is inaccurate, and is sensitive to the purity of the radical solution; *e.g.*, if Selwood's solution was only 70% as concentrated as he thought, there would be no correction on his susceptibility. The assumption that his radical was 100% pure requires an average diamagnetic exaltation for this radical of $-0{\cdot}19 \pm 0{\cdot}14 \times 10^{-6}$ cm^3 g^{-1}. The uncertainty in determining this value is evident and the average value is probably much too large a number for the actual diamagnetic exaltation of the radical.

The diamagnetic susceptibility calculation for the dimer is structure sensitive, and the revision in structure[8] requires that the results be recalculated. The table shows the results of the recalculation using Pascal's constants from Haberditzl.[9] The last column also applies the above crudely calculated correction on the monomer susceptibility, assuming that it is uninfluenced by the t-butyl groups. Several conclusions appear:

(1) The discrepancy between the magnetic and spectrophotometric measurements has virtually disappeared. (2) The erroneous dimer structure is principally responsible for this long-standing discrepancy between the two methods of measurement. (3) There is a possibility of an error in the diamagnetic component of the radical susceptibility, but it is not a major source of error in the magnetic measurement, except possibly when the degree of dissociation is large. (4) We cannot correct magnetically measured reported degrees of dissociation of any substituted trityl dimers until the dimer structure is known. However, many of the peculiar effects of substituent can now be seen to be effects of variation in dimer structure.

We thank the Robert A. Welch Foundation for support.

(*Received*, 3*rd February* 1975; *Com.* 123.)

[1] K. Ziegler and L. Ewald, *Annalen*, 1929, **473**, 163.
[2] E. Müller and I. Müller-Rodloff, *Annalen*, 1935, **521**, 89.
[3] R. Preckel and P. W. Selwood, *J. Amer. Chem. Soc.*, 1941, **63**, 3397.
[4] M. Roy and C. S. Marvel, *J. Amer. Chem. Soc.*, 1937, **59**, 2622.
[5] G. E. Wheland, 'Advanced Organic Chemistry,' 2nd edn., Wiley, New York, 1949, p. 695.
[6] C. S. Marvel, M. B. Mueller, C. M. Himel, and J. F. Kaplan, *J. Amer. Chem. Soc.*, 1939, **61**, 2771.
[7] P. W. Selwood and R. M. Dobres, *J. Amer. Chem. Soc.*, 1950, **72**, 3860.
[8] H. Lankamp, W. T. Nauta, and C. Maclean, *Tetrahedron Letters*, 1968, 249.
[9] W. Haberditzl, *Sitzber, Deut. Aka. Wiss. Berlin, Kl. Chem. Geol., Biol.*, 1964, 2.