kcal. consequently may be deduced. Thus values for ΔE range from 21 to 80 kcal., and, therefore, the estimated energy of rupture of the newly formed B–O bond in the etherate ranges from 34 to 93 kcal. In similar fashion, one may deduce from the observed heat of reaction

$$C_5H_5N:BF_3(g) = BF_3(g) + C_5H_5N(g), \ \Delta H = 51 \text{ kcal.}^{20}$$

that the energy of rupture of the B–N bond is somewhere between 72 and 130 kcal. These values, rough as they are, clearly demonstrate that the bonds formed in this type of association reaction are comparable in strength to those of normal covalent bonds between the corresponding atoms.[21] In contrast, the maximum dipole–dipole energy, say for dimethyl ether–boron trifluoride, is around 15 kcal. Thus, unless it is shown that the magnitude of the ordinary polarization forces is several times that of the dipole–dipole interaction, the view that a definite chemical bond is formed is distinctly favored, and in a number of cases appears to be the only one which is acceptable; one such example is the association of two $Al(CH_3)_2X$ molecules to produce a unit of zero moment.

Summary

An electron diffraction investigation of the compound dimethyl ether–boron trifluoride $[(CH_3)_2O:BF_3]$ led to the following structure for this molecular compound: the boron valence angles are tetrahedral; B–F = 1.41 ± 0.02 Å.; B–O = 1.52 ± 0.06 Å.; the dimethyl ether part of the molecule remains essentially unaffected; at most, the C–O separation being stretched from 1.42 to 1.44 Å. Although the available photographs agree best with the assumption that the oxygen valence angles are tetrahedral, the possibility that the ∠BOC's and even ∠COC are 120° cannot be definitely eliminated.

The energetics of the association reaction is discussed and, on the basis of values estimated, it is suggested that the bond formed in the association process be regarded as being due to an electron pair rather than to dipole–dipole interaction.

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for the latter is 147 kcal. (ref. 14, p. 53). (b) From the structural data, and the curve proposed by Pauling (ref. 14, p. 164), the bond order in boron trifluoride is roughly 0.3. If the strength of a double bond is assumed to be about 1.7 times that of a single bond, one gets 130–140 kcal. for the strength of the B–F single bond, depending on the ΔH selected for the energy of formation of BF_3. (c) On combining the equation given in ref. 18 with the following

$F(g) + e^- = F^-(g)$, $\Delta H = -95$ kcal. (ref. 14, p. 322)
$B(g) + e^- = B^-(g)$, the electron affinity of boron must be less than 5 kcal., and hence negligible in the following argument
$BF_3(g) + F^-(g) = BF_4^-(g)$, $\Delta H = -71$ kcal.

(J. H. de Boer and J. A. M. van Liempt, *Rec. trav. chim.*, **46**, 124 (1927) one may deduce

$$B(g) + 3F(g) + F^-(g) = BF_4^-(g), \ \Delta H = -577 \text{ kcal.}$$
$$B^-(g) + 4F(g) = BF_4^-(g), \ \Delta H = -670 \text{ kcal.}$$

Now, the strength of the B–F single bond is one-fourth of a value somewhere between the two given above, being closer to the first than to the second. A judicious guess is 600/4 = 150 kcal.

[20] P. A. van der Meulen and H. A. Heller, THIS JOURNAL, **54**, 4404 (1932). Doctoral Dissertation by G. R. Finlay

$$BF_3(g) + NH_3(g) = H_3N:BF_3(s), \ \Delta H = -42 \text{ kcal.}$$

which checks with the value given, when a reasonable energy of sublimation is added to the 42 kcal.

[21] One should not forget that the donating and accepting properties of the atoms involved and thus the bond strength will depend on the nature and steric factors of the groups attached to them. For instance, compare the ΔH given for the association of ammonia–boron trifluoride with

$$B(CH_3)_3(g) + NH_3(g) = H_3N:B(CH_3)_3(g), \ \Delta H = -8 \text{ to } -10 \text{ kcal.}$$

Computed from data of A. Stock and F. Zeidler, *Ber.*, **54**, 531 (1921). The influence of steric factors is discussed in ref. 15.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Disproportionation of *o*-Tolyldiphenylmethyl

BY P. W. SELWOOD AND RALPH F. PRECKEL

Marvel[1] and his co-workers have recently in several publications drawn attention to the disproportionation of hexaarylethanes to form substituted methanes and olefinic compounds, with the consequent disappearance of the free radical. A previous communication[2] by the authors points out the significance of disproportionation toward colorimetric and ebullioscopic determinations of free radical concentration. In an effort to learn more of the mechanism of the disproportionation reaction the following work was undertaken. It consists of parallel magnetic, spectroscopic, and ebullioscopic measurements on di-*o*-tolyltetraphenylethane undergoing disproportionation in benzene solution.

Experimental

The magnetic measurements and the preparation of the free radicals have already been described.[3] Again the

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[1] Marvel, Rieger and Mueller, THIS JOURNAL, **61**, 2769 (1939), *et seq.*

[2] Preckel and Selwood, *ibid.*, **63**, 3397 (1941).

authors are indebted to Professor C. S. Marvel of the University of Illinois for supplying the triarylmethyl chloride.

In an earlier paper the method of calculating free radical concentrations and apparent degrees of dissociation from the magnetic data is given. That paper contains an error in that the quantity given as α, the degree of dissociation, is incorrect. The true degree of dissociation in that paper is given by $2\alpha/(1 + \alpha)$. This unfortunate error will be corrected in an early communication. The heats of dissociation of the ethanes given are but little changed by the correction, although there are some changes in the entropies.

Spectroscopic Measurements.—A jacketed absorption cell about 2.5 cm. long, shown in Fig. 1, was sealed off under vacuum with suitable amounts of frozen benzene, *o*-tolyldiphenylmethyl chloride, and molecular silver. This cell had quartz windows sealed with silver chloride. The temperature of the cell was maintained at 80° by distilling benzene through the jacket. A small Bausch and Lomb Littrow spectrograph was used. The light source was a microscope lamp. It was possible to follow the entire course of disproportionation over about forty hours, with 20 exposures on a single plate. The procedure generally used was to photograph the spectrum of the solution at room temperature, then at 80° as disproportionation proceeded, then finally at room temperature again. So as to have several reference lines available on each photograph a solution of europium nitrate was placed just before the slit. The europium ions in solution give a few sharp bands which serve as points of reference.

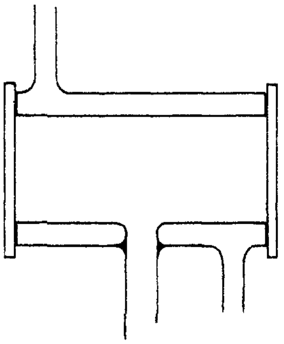


Fig. 1.—Jacketed absorption cell.

The various spectrograms were then run through a microphotometer to obtain the relative density of plate blackening as a function of wave length. The absorption intensity is given in arbitrary percentage units in Fig. 6.

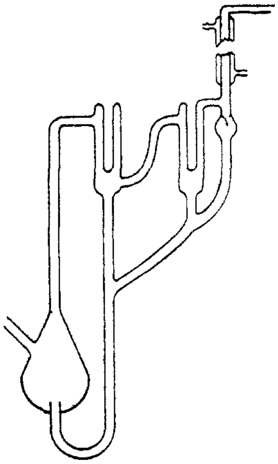


Fig. 2.—Swietoslawski type differential ebulliometer.

Ebullioscopic Measurements.—The ebulliometer used was of a Swietoslawski differential design as shown in Fig. 2, thoroughly insulated with fireproof (Christmas tree) cotton. The two wells were partly filled with mercury in which the opposite ends of an eight-junction copper-constantan thermocouple were placed. The ends of the individual couples were encased in thin glass tubes partly filled with mercury to eliminate air spaces. The potential developed between "hot" and "cold" wells was measured by a potentiometer and a high sensitivity galvanometer. A sensitivity of 0.1 microvolt was attainable, but the instrument was seldom steady to better than 2 microvolts. For a 0.05 molal solution of ethane in benzene the tolerance in observed molecular weight was about ±4%. This accuracy limit was checked by use of known solutions such as triphenylmethane in benzene, but considerable experience and care were necessary before the results could readily be duplicated. The measurements were made under one atmosphere of pure, dry nitrogen, elaborate precautions being taken to prevent access of air or moisture.

Results

Magnetic measurements on benzene solutions of di-*o*-tolyltetraphenylethane were made at 80 and at 95°. The data, which were in some cases obtained over a period of four days, are shown in Fig. 3, which shows actual free radical concentrations plotted against time. For the run at 80° the initial over-all ethane concentration was 0.0517 M and for that at 95°, 0.0714 M. Dissociation was nearly 90% complete at the beginning of each run. Figure 4 shows $1/[R_3C]$, or the reciprocal of free radical concentration plotted against time. For the 80° run the reaction is clearly second-order with respect to free-radical concentration. This does not, however, prove that disproportionation takes place through the free radical, rather than through the ethane. In Fig. 4 $[R_3C]$ is not corrected for the small amount of undissociated ethane in solution. This is justifiable, because even at the beginning of the run only 10% of the ethane is

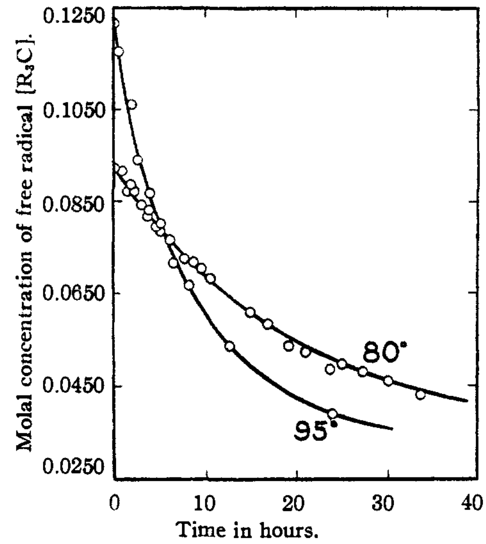


Fig. 3.—Rate of disproportionation of *o*-tolyldiphenylmethyl in benzene at 80 and at 95°.

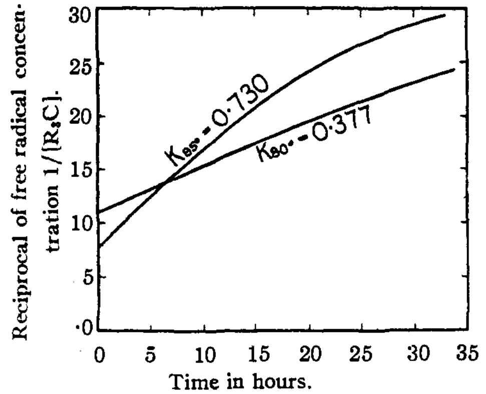


Fig. 4.—Second-order velocity constants for the disproportionation of *o*-tolyldiphenylmethyl.

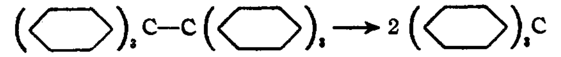
present as such, and as disproportionation proceeds it must become less. The reaction at 95° is also clearly second-order, except when most of the free radical has been destroyed.

Second-order velocity constants taken over the earlier hours of the reaction are 0.377 at 80° and 0.730 at 95°. From these the activation energy for the disproportionation of *o*-tolyldiphenylmethyl

$$E = 2.303\,R\left(\frac{T_2T_1}{T_2 - T_1}\right)\log\frac{k_2}{k_1}$$

is 11.4 kcal. per mole of free radical. It is a coincidence that this is exactly the same as the heat of dissociation of the corresponding ethane.

Measurements by others[3,4,5] who have studied the rate of dissociation of hexaphenylethane lead to the value 19 kcal. for the activation energy of the reaction



It would be interesting to have some magnetic data on the rate of dissociation at different temperatures. Assuming that 19 kcal. is approximately correct for the activation energy, we may summarize the energy relationships between the reversible and the irreversible reactions of a free radical as in Fig. 5.

Results of the spectroscopic study are shown in Fig. 6. The most interesting results become apparent only at low concentrations. The top two curves show the absorption at 25 and at 80° after fairly rapid heating. The changes so produced are thermally reversible. But as the temperature is held at 80° some very marked changes occur in the blue. Finally all the structure and bands originally present between 4200 and 5300 Å. disappear. At the end of four days of heating, when disproportionation must be complete, the spectrum in the blue is not only greatly changed, but it has become independent of temperature, as is shown in the two bottom curves. But during these changes the intense broad band in the orange and red suffers no change whatever.

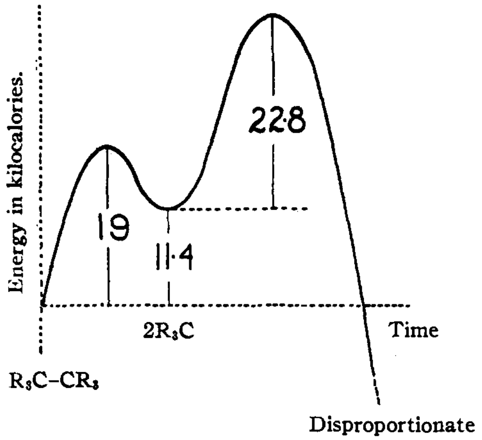


Fig. 5.—Energy relationships between reversible and irreversible reactions of *o*-tolyldiphenylmethyl.

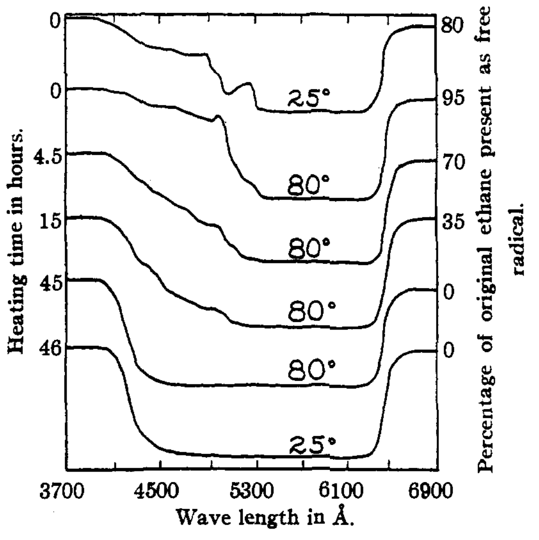


Fig. 6.—Absorption spectrum of *o*-tolyldiphenylmethyl at various temperatures and stages of disproportionation. Ordinates are in arbitrary units of absorption.

It has already been pointed out that one of the most interesting phenomena associated with disproportionation of *o*-tolyldiphenylmethyl is that the color does not change. This effect is now seen to be an optical illusion based upon the persistence of the intense band in the orange and red. Although colorimetric methods have

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(3) Ziegler, Orth and Weber, *Ann.*, **504**, 131 (1933).

(4) Ziegler and Ewald, *ibid.*, **504**, 162 (1933).

(5) Mithoff and Branch, THIS JOURNAL, **52**, 255 (1930).

been shown to be misleading for the study of free radicals, it may be possible to develop accurate spectrophotometric methods, based on the bands in the blue, for this purpose. Further studies along this line are being undertaken.

The effect described is masked at higher concentrations. For instance, through a 2.5-cm. layer of 0.03 *M* solution the only change observed during disproportionation was a shift toward longer wave length of the region of general absorption in the blue.

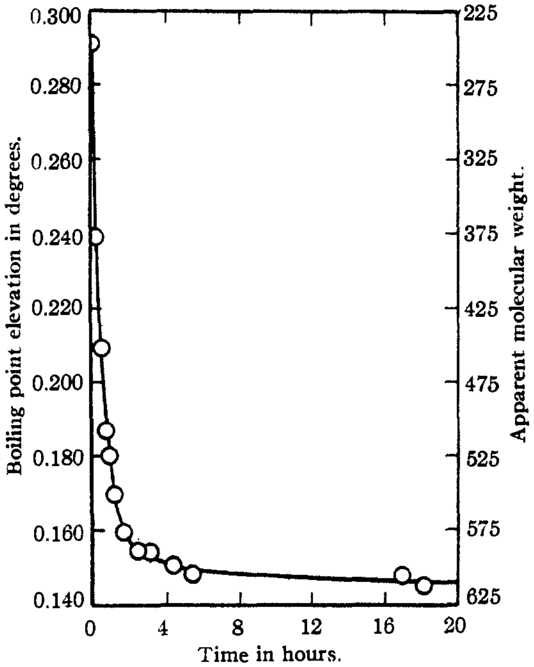
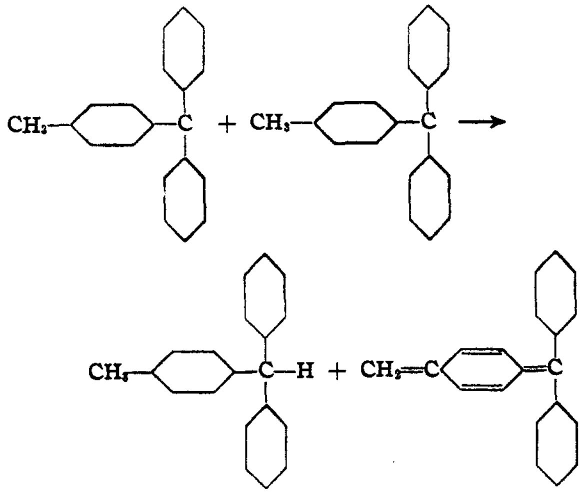


Fig. 7.—Time dependence of boiling point elevation produced by a 0.0557 *M* solution of di-*o*-tolyltetraphenylethane in benzene.

An example of the results obtained with the ebulliometer is shown in Fig. 7. This gives the temperature differential and the approximate apparent molecular weight for a 0.0557 *M* solution of di-*o*-tolyltetraphenylethane in benzene solution at the normal boiling point. The measurements were extended over eighteen hours. At first the molecular weight was approximately that expected for an ethane, 80 to 90% dissociated. But the apparent molecular weight increased very rapidly, and this much more rapidly than the free radical concentration might be expected to decrease according to the magnetic measurements. Thus, at the end of one and a half hours the apparent molecular weight has more than doubled. The magnetic data, on the other hand, indicate that the solution should still contain over 80% of the original ethane in the form of free radical. It is possible that disproportionation in the ebulliometer proceeds much more rapidly than in the magnetic balance. This might be due to the rapid stirring caused by the boiling in the former, and possibly to the light of the little gas flames used to maintain boiling. Probably no quantitative significance should be attached to the ebulliometric results. Qualitatively it is seen that boiling point methods are not reliable for determination of free radical concentration, that the apparent molecular weight increases rapidly and then after a few hours becomes constant at a value in the neighborhood of that for the original undissociated ethane. The color of the solution in the ebulliometer did not change.

The disproportionation mechanism suggested by Marvel for *p*-tolyl radicals involves formation of an "activated vinyl" type quinoid followed by



polymerization. The polymer is colorless. But for the series above methyl the color remains, as is the case for *o*-tolyl radicals. This is assumed to be because the quinoid hydrocarbon does not polymerize unelss the substituent is a *p*-methyl group.[6] This explanation fits the data presented here except in respect to the apparent molecular weight which should remain constant or even decrease slightly instead of doubling. The doubled molecular weight is evidence that polymerization does take place even for *o*-tolyl radicals. The peculiar spectroscopic results suggest that the bands in the blue, whose intensity clearly

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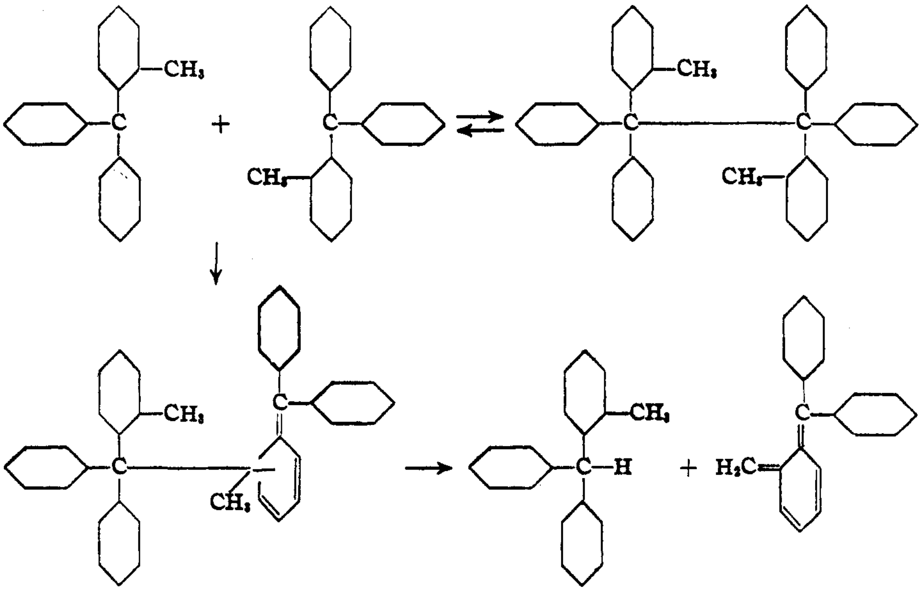
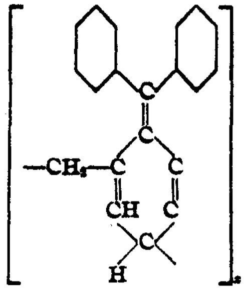
(6) Marvel, Mueller, Himel and Kaplan, THIS JOURNAL, 61, 2771 (1939).

parallels the free radical concentration, may be due to a para-quinoid structure, while possibly the persistent band in the red may be due to ortho-quinoid structures. Additional spectroscopic work on *p*-substituted and on other free radicals is being undertaken.

The meta-substituted free radicals appear to be about as stable toward disproportionation as triphenylmethyl. This fact, together with the reaction order, supports Marvel's mechanism. While we are unable as yet to give the final stage of the disporportionation reaction, the main features of both reversible and irreversible reactions of *o*-tolyldiphenylmethyl are probably represented below.



The authors are indebted to the Referee for pointing out that polymerization of the *o*-quinoid structure might concern the side chain methylene and the adjacent ring unsaturation. The recurring unit might be



in which case the *p*-quinoid structure would be retained.

Summary

A parallel magnetic, spectroscopic and ebullioscopic study has been made of the disproportionation of *o*-tolyldiphenylmethyl in benzene at 80°. The reaction gives a second-order velocity constant, with an activation energy of 11.4 kcal. During disproportionation several absorption bands in the blue are eliminated, while a large band in the orange and red remains unchanged. The spectrum is temperature dependent before disproportionation, but not after. The apparent molecular weight approximately doubles during disproportionation, but this occurs much more rapidly than is to be expected from the magnetic data. Possible disproportionation mechanisms are presented.

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