**Tetrahedron Letters No.27, pp. 3147-3151, 1966. Pergamon Press Ltd.
Printed in Great Britain.**

SOLVENT EFFECTS ON FREE RADICAL FORMATION.
THERMOLYSIS OF PHENYLAZOTRIPHENYLMETHANE

Wesley G. Bentrude and Allen K. MacKnight

Department of Chemistry, University of Utah
Salt Lake City, Utah

(Received 28 April 1966)

The role played by solvent in the reactions of organic molecules is not well understood. One is often tempted to try to interpret solvent effects on processes in which ions or molecules are formed solely in terms of solvent interactions with an ionic or radical-like transition state to the neglect of the possible contributions of ground-state factors. The importance of ground-state considerations in ion formation in certain solvolyses has, however, recently been amply demonstrated by Arnett and coworkers[1]. We wish to report results from a study of a free radical dissociation in which both ground- and transition-state effects seem to require interpretation.

The reaction studied is the thermal decomposition of phenylazotriphenylmethane, I.

$$\underset{\text{I}}{(C_6H_5)_3C\text{-}N\text{=}N\text{-}C_6H_5} \xrightarrow[\Delta]{} (C_6H_5)_3C\cdot + N_2 + C_6H_5\cdot$$

We have dissected the solvent-related variations in activation enthalpy*,

---

*These values covered a range of 4.5 kcal/mole in $\Delta H^{\ddagger}$ and 14 e.u. in $\Delta S^{\ddagger}$, and we consider these variations to be beyond experimental error. For a discussion of error in enthalpy-entropy relations see J. E. Leffler, *J. Org. Chem.* **31**, 533 (1966).

$\delta_M\Delta H_s^{\ddagger}$, (determined by Leffler and Alder[2] from kinetic measurements at 25-75°C), into ground- and transition-state components. This was accomplished by measuring calorimetrically* the partial molal heats of solution, $\Delta\bar{H}_s^g$ for I at 25°C in the same solvents in which $\Delta H_s^{\ddagger}$ had been determined. The variation in $\Delta\bar{H}_s^g$, $\delta_M\Delta\bar{H}_s^g$, is then a measure of the relative ground-state enthalpy of I in the several solvents. The relative transition state enthalpies, $\delta_M\Delta\bar{H}_s^t$ are then found using the equation**

$$\delta_M\Delta H_s^{\ddagger} = \delta_M\Delta\bar{H}_s^t - \delta_M\Delta\bar{H}_s^g$$

The data appear in Table 1 and are presented graphically in Figure 1. (Variations in $\Delta\bar{H}_s^g$, $\Delta\bar{H}_s^t$, and $\Delta H_s^{\ddagger}$ are all relative to value in benzene).

TABLE I. ACTIVATION ENTHALPIES AND ENTROPIES; SOLUTION HEATS FOR PHENYLAZOTRIPHENYLMETHANE

Solvent	$\Delta H_s^{\ddagger}$ (a)	$\Delta S_s^{\ddagger}$ (a)	$\Delta\bar{H}_s^g$ (b)
cyclohexane	24.5 ± 0.1	-1.16 ± 0.4	7.09 ± 0.15
benzene	26.8 ± 0.1	6.57 ± 0.3	4.38 ± 0.09
diethylmalonate	27.9 ± 0.15	9.7 ± 0.4	5.62 ± 0.07
chlorobenzene	28.3 ± 0.1	11.4 ± 0.4	5.02 ± 0.04
nitrobenzene	28.4 ± 0.25	11.2 ± 0.8	6.09 ± 0.19
anisole	28.8 ± 0.2	12.5 ± 0.2	4.99 ± 0.06
benzonitrile	29.0 ± 0.3	13.4 ± 0.9	5.18 ± 0.13

(a) Values from ref. 1.

(b) Endothermic partial molal heats of solution, kcal/mole; errors are average deviations based on at least five determinations.

---

*The calorimeter and method used were essentially the same as that described in reference 1.

**See ref. 1 for a more complete derivation of this expression.

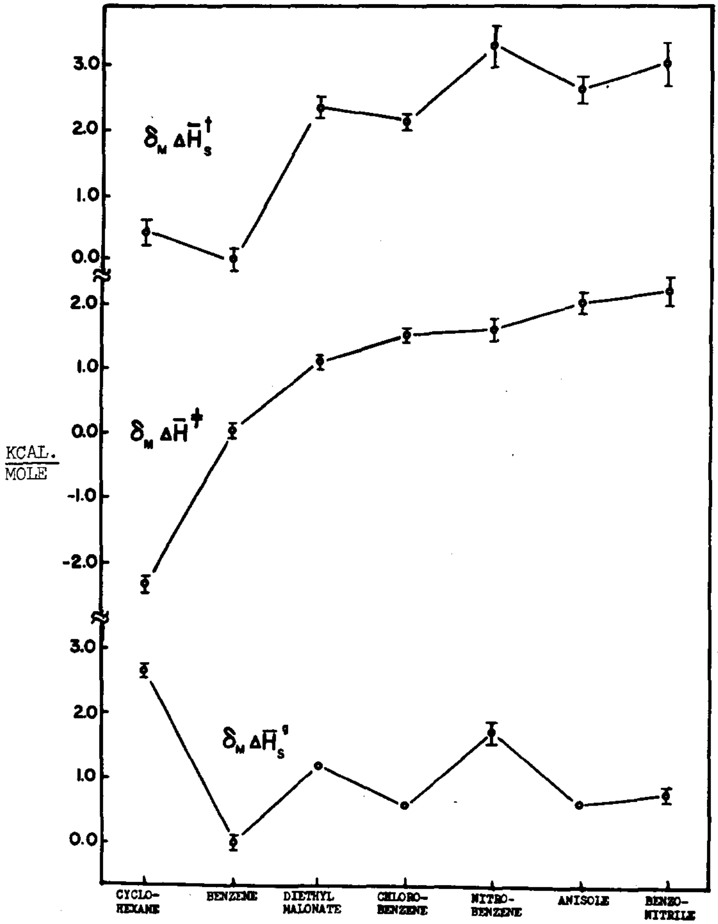

Figure 1. Dissection of solvent effects on enthalpy factors for phenylazotriphenylmethane decomposition. (All enthalpy variations are taken relative to value in benzene as zero.)

Although we are unable at this time to analyze these trends, it should be noted that both $\delta_M\Delta H_s^g$ and $\delta_M\Delta H_s^t$ are important in the determination of $\delta_M\Delta H_s^\ddagger$ and must be considered in any explanation. In fact, the large increase in $\Delta H^\ddagger$ on transfer from cyclohexane to benzene is totally a result of an increase in ground-state stability, since ΔH_s^t is constant within experimental error. In contrast, the gentle overall increase going from diethylmalonate to benzonitrile is largely a transition state effect. The gain in $\Delta H_s^\ddagger$ from benzene to diethyl malonate arises from enthalpy increases of differing magnitudes in both states.

Leffler and Alder[2] recognized the possible importance of ground state effects and actually postulated a desolvation mechanism of activation. As we understand their work, this would attribute the solvent effects entirely to ground state solvation variations. Based on our data it is not possible, for the reasons that follow, to accurately evaluate this proposal. The net heat of solution in any case has at least two important components. One results from destruction of solute-solute interactions as the solute enters the solvent. The other stems from the solute-solvent interaction----solvation. (There is always a lattice term as well but which is constant for a given solute from solvent to solvent). Therefore, even complete desolvation (loss of the solvent-solute interaction component of $\Delta\bar{H}_s^t$) would not lead to a constant value of $\Delta\bar{H}_s^t$ as might be at first predicted, since the solute-solute interactions to be overcome by the transition state on entering the solvent would be different from solvent to solvent.

In most cases $\Delta H_s^\ddagger$ and $\Delta S_s^\ddagger$ for radical formation for most other well known initiator molecules have been shown to be relatively insensitive to solvent changes[3] (in the absence of induced decomposition). There are, however, some notable exceptions[4]. It is hoped that reasons for these exceptions as well as a better understanding of the relative importance of π-complexing[5], solvent polarity[6] and hydrogen bonding[7] on radical reactions will be forthcoming from further studies of the type we report. More extensive comment on the relation of our results to these problems is reserved until more data are available.

Acknowledgment. It is a pleasure to acknowledge support of this research through grants from the Research Corporation, the National Science Foundation (GP-3772) and University of Utah Research Fund.

REFERENCES

1. E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, J. Am. Chem. Soc., 87, 1541 (1965).

2. M. G. Alder and J. E. Leffler, J. Am. Chem. Soc., 76, 1425 (1954).

3. E. g., t-butyl perbenzoate (5 solvents), A. T. Blomquist and A. F. Ferris, J. Am. Chem. Soc., 73, 3412 (1951); benzoyl peroxide (12 solvents), A. T. Blomquist and A. J. Buselli, ibid., 73, 3883 (1951) and refs. cited therein; azobisisobutyronitrile (4 solvents), R. C. Peterson, J. H. Markgraf and S. D. Ross, ibid., 83, 3819 (1961); di-t-butyl peroxide (3 solvents), J. H. Raley, F. F. Rust and W. E. Vaughn, ibid., 70, 1336 (1948); acetyl peroxide (5 solvents) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 492.

4. (a) D. L. Tuleen, W. G. Bentrude, and J. C. Martin, J. Am. Chem. Soc., 85, 1938 (1963); (b) R. C. Lamb, F. F. Rogers, Jr., G. D. Dean, Jr., and F. W. Boight, Jr., ibid., 84, 2635 (1962); (c) M. G. Alder and J. E. Leffler, ibid., 76, 1425 (1954); (d) M. D. Cohen, J. E. Leffler and L. M. Barbato, ibid., 76, 4169 (1954); (e) W. Honsberg and J. E. Leffler, J. Org. Chem., 26, 733 (1961).

5. C. Walling and F. Mayahi, J. Am. Chem. Soc., 81, 1485 (1959); M. M. Martin and C. J. Gleicher, ibid., 86, 238 (1964); G. A. Russell, ibid., 80, 4987 (1958) and later papers.

6. C. D. Cook and B. E. Norcross, J. Am. Chem. Soc., 81, 1176 (1959); D. G. Hendry and G. A. Russell, ibid., 86, 2368 (1964); C. Walling and P. J. Wagner, ibid., 86, 3368 (1964).

7. C. Walling and P. J. Wagner, J. Am. Chem. Soc., 86, 3368 (1964); F. F. Rust and E. A. Youngman, J. Org. Chem., 27, 3778 (1962).