



using the standard Hammett equation treatment utilizing  $\sigma$  substituent constants.<sup>6</sup>

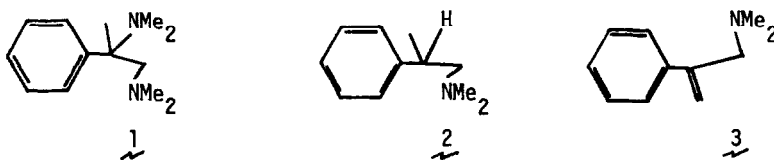
TABLE I

Addition of Zinc Chloride Complexed Dimethylamino  
Radicals to  $\alpha$ -Methylstyrenes

$\alpha$ -Methylstyrene	$\log k/k_0$	$\sigma$
p-OCH <sub>3</sub>	0.376	-0.268
p-CH <sub>3</sub>	0.256	-0.170
p-F	0.009	0.062
p-H	0.0	0.0
p-Br	-0.175	0.232
p-Cl	-0.210	0.227
p-CN	-0.540	0.660

The straight line obtained from a least squares fit of the data in Table I, had a correlation coefficient of .99 and yielded a  $\rho$ -value of  $-0.98 \pm .04$ . These data indicate that the zinc chloride complexed amino radical is moderately electrophilic in the addition reaction to the olefinic bond of  $\alpha$ -methylstyrene. That is, electron attracting substituents destabilize the transition state, while the converse is true for electron donating substituents.

We now turn to the uncomplexed amino radicals. Photolysis of degassed solutions of tetramethyl-2-tetrazene in cyclohexane in the presence of substituted  $\alpha$ -methylstyrenes resulted in the formation of 1, 2 and 3 in low yields (10% of 1 and ca. 5% of 2 and 3) together with large quantities of tetramethylhydrazine and dimethylamine and various other minor (<1%) products.



Attempts to obtain relative rate correlations using product 2 failed because it was difficult to separate it cleanly from the other products by glc and because its yield was very small in the case of some of the substituted styrenes. The same was true for product 3 (which had the other disadvantage of being formed by more than one path).<sup>7</sup> Product 1 was easily determined quantitatively versus an internal standard (biphenyl) and consequently the relative yields of 1 were used to calculate the relative rates of addition of the dimethylamino radical to substituted

-methylstyrenes. Table II presents the relative rate data, together with the relevant constants.

TABLE II  
Addition of Dimethylamino Radicals to  $\alpha$ -Methylstyrenes

$\alpha$ -Methylstyrenes*	log k/k <sub>0</sub>	$\rho$
p-OCH <sub>3</sub>	-0.421	-0.268
p-CH <sub>3</sub> <sup>3</sup>	-0.196	-0.170
p-H <sup>3</sup>	0.0	0.0
p-F	0.028	0.062
p-Cl	0.139	0.227
p-CN	0.408	0.660

\* The p-Br styrene gave erratic values, presumably due to the photolability of the product and/or reactant.

The Hammett equation correlation of the data in Table II yielded  $\rho$ -value of  $+0.69 \pm 0.03$ . The correlation coefficient was 0.99. The positive  $\rho$ -value indicates that the uncomplexed radical, in contrast to the complexed one, is nucleophilic in the addition reaction to styrene.

A question remains whether it is valid to use the rate of formation of a product which is formed in low yield to measure the reactivity of dimethylamino radical? It is our contention that the experiment is valid, for the following reasons. First, the correlation obtained is an excellent one and the data are highly reproducible. Second, although the attempted correlation using product 2 was not very good, the trend of the values obtained was in the correction direction, i.e. the best yields were obtained with styrenes substituted by electron attracting substituents. Third, when the dimethylamino radical was allowed to compete for styrene and p-chloro-styrene, the substituted compound reacted faster (by a factor of 1.5), again consistent with the data for  $\alpha$ -methylstyrenes. Thus, we conclude that the correlation reported in this paper is real and the dimethylamino radical (and presumably other amino radicals) can be either electrophilic or nucleophilic, depending on the type of reaction. This seems to be the first example of a simple radical displaying nucleophilic properties in an addition reaction.<sup>8</sup>

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REFERENCES AND FOOTNOTES

1. This is paper IV dealing with metal-complexed amino radicals. Paper III is C. J. Michejda and D. H. Campbell, J. Amer. Chem. Soc., 98, 6728 (1976).
2. C. J. Michejda and W. P. Hoss, J. Amer. Chem. Soc., 92, 6298 (1970).
3. C. J. Michejda and D. H. Campbell, ibid., 96, 6298 (1974).
4. The mechanistic details of this reaction will be published, cf. D. H. Campbell, PhD Thesis, University of Nebraska, 1975.
5. cf. I. H. Sadler, J. Chem. Soc., (B), 1024 (1969).
6. The rates could also be correlated using  $\sigma^+$  constants. For the purposes of the discussion, however, it is pointless to assume that one set of substituent constants is more appropriate than the other since it is only the direction of the slope (the  $\rho$ -value) which is important, rather than its absolute magnitude. It might be pointed out, however, that if our spread in  $\sigma$ -values were larger, we might have observed significant differences in the correlation.
7. Product 3 can be formed by disproportionation of the intermediate  $\beta$ -dimethylamino- $\alpha$ -methylstyryl radical, or it can be the result of first, H-atom abstraction from methylstyrene, followed by the combination of the styryl radical with a dimethylamino radical. Likewise, product 2 can be a result of at least two paths.
8. The abstraction of the H-atoms from toluene by the t-butyl radical also shows a positive  $\sigma\rho$  correlation. W. A. Pryor, W. H. Davis, Jr. and J. P. Stanley, J. Amer. Chem. Soc., 95, 4754 (1973).