Aromatic Diazothio-ethers

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WE are investigating the behaviour of aromatic thiyl radicals and report on diazothio-ethers (I) as a source of these fragments, particularly as regards substituent effects on rates of decomposition:

$$\underset{\text{(I)}}{X{\cdot}C_6H_4{\cdot}N{=}N{\cdot}S{\cdot}C_6H_4{\cdot}Y} \rightarrow N_2 + X{\cdot}C_6H_4{\cdot} + {\cdot}S{\cdot}C_6H_4{\cdot}Y$$

Compounds (I) may readily be prepared[1] by adding a solution of a diazotised aniline, neutralized with sodium carbonate, to an ice-cold alkaline solution of the thiol; yields are practically quantitative.

Reynolds and Cotten[2] have reported that these substances are capable of initiating styrene–butadiene polymerization and that substituents have an enhancing or retarding effect on initiation, depending on whether they are electron-repelling or -withdrawing, respectively.

In support of the view that the decomposition consists of a homolytic fission into the above fragments, we observed that toluene is formed when (I) ($X = p$-Me; $Y = p$-Bu^t) is decomposed is isopropylbenzene, whereas the use of 9,10-dihydroanthracene as a scavenger resulted in the formation of p-t-butylthiophenol. Nitrogen evolution amounted to more than 95% of the theoretical volume.

Decomposition reactions of various compounds (I) were carried out in the absence of light so as to avoid the rapid photodecomposition taking place even in diffuse daylight. Rates were determined spectrophotometrically at wavelengths dependent on the initial concentration (10^{-3}—10^{-4} M). They were not affected by oxygen. In all cases studied, except that with $X = p$-Me; $Y = p$-NO$_2$, the reactions were first order, the rate constants being independent of initial concentrations. This suggests that no induced decomposition took place. Data are given in the accompanying table. The high reactivity of the mesitylene derivative is probably due to non-planarity and the concomitant loss of conjugation energy. Substituents X appear to have a weaker effect than substituents Y, presumably because of the fact that the N–S bond should be the weakest in the system and is closer to Y than to X. The stabilizing effect of p-NO$_2$, both as X and as Y, could be due to its capability of stabilizing resonance hybrids involving the $N{=}S^+$ bond; the influence of p-OMe—stabilizing as X, destabilizing as Y—seems less obvious. In any case, the importance of conjugation transpires from the correlation between substituent effects on rates and those on the u.v. maximum; thus, longer wavelengths generally correspond to lower rates! The rate-depressing effect of p-OMe in the X-position may be weakened by stabilization of the p-MeO–C$_6$H$_4\cdot$ radical, as suggested by Cohen and Wang for the case of substituted phenylazotriphenylmethanes[3]).

The activation parameters for decomposition of (I; $X = p$-Me; $Y = p$-Bu^t) were determined from rate measurements over the temperature range 46—66° and found to be 36·7 kcal and 34·8 e.u.

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[1] A. Hantzsch and H. Freese, *Ber.*, 1895, **28**, 3237.
[2] W. B. Reynolds and E. W. Cotten, *Ind. Eng. Chem.*, 1950, **42**, 1905.
[3] S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, 1953, **75**, 5504.

Properties of some substituted aromatic diazothio-ethers

X ($-C_6H_4{\cdot}N{=}N{\cdot}S{\cdot}C_6H_4-$) Y		λ_{max} (mμ)	log ϵ	m.p.*	First order rate constant** (benzene solution, 55·5°) × 10^5 (sec.$^{-1}$)
X	Y				
H	p-Bu^t	336	4·03	33·5—34·5	8·3
p-Me	,,	339	4·10	58·5—59·5	8·8
p-OMe	,,	348	4·20	50—51	6·8
p-NO_2	,,	355	4·10	73—74	0·95
2,4,6-trimethyl	,,	328	—	<0	116
p-Me	H	340	—	<0	5·0
,,	p-OMe	334	4·12	36·5—37	67
,,	p-NO_2	360	4·24	70—71	0·25†

* Uncorrected. n.m.r. spectra (Varian A60) and sulphur contents agreed with data expected for the compounds named.** Accuracy probably better than 5%.† Extrapolated from data at higher temperatures; the value tabulated should be regarded as an upper limit because of some induced decomposition taking place even at the high dilutions employed (10^{-4} M).

The high value for the activation entropy may be attributable to the gain of degrees of freedom which should accompany the formation of three fragments from the originally rigid azo-compound.

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