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ESR Study of the Formation of $SO_2^{\overline{\cdot}}$ in the Pyrolysis of Sodium Bisulfite Adducts of Aldehydes and Ketones

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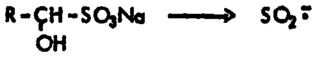
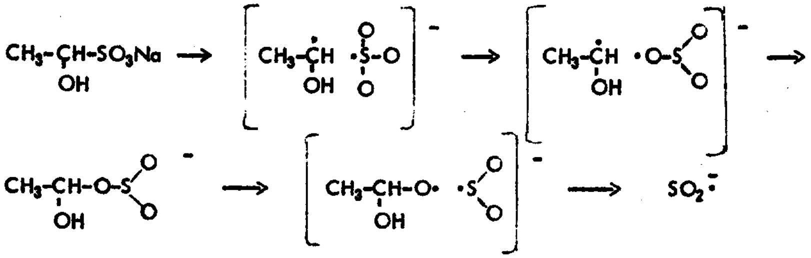
We have found sodium bisulfite addition products of aldehydes and ketones decompose as polycrystalline solids to form $SO_2^{\overline{\cdot}}$ when heated at moderate temperatures:



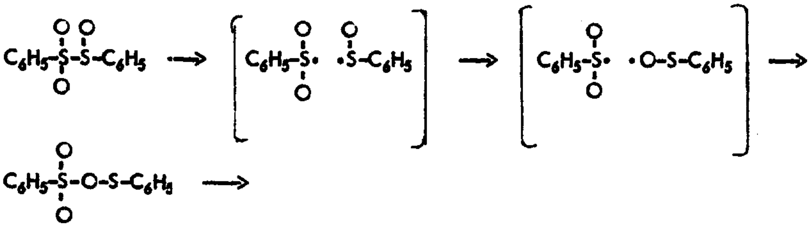
$$R-\underset{OH}{CH}-SO_3Na \longrightarrow SO_2^{\overline{\cdot}}$$

For example, the sodium bisulfite addition product of acetaldehyde produces readily detectable amounts of free radicals at temperatures above 90°. The amount of free radicals increases with increase in temperature to 140° but almost immediately attains a steady state value at any given temperature. The g-value of the radical produced was found to be 2.0057 using DPPH (g-value 2.0036) as a standard. Since the g-values of $SO_2^{\overline{\cdot}}$ and $SO_3^{\overline{\cdot}}$ are 2.0057 and 2.0036 respectively (1,2) we conclude that the radical detected by e.s.r. is $SO_2^{\overline{\cdot}}$. No hyperfine splitting can be observed for these radicals in polycrystalline samples. The assignment of the $SO_2^{\overline{\cdot}}$ structure to the radical is based on 1) g-value 2) the known stability of $SO_2^{\overline{\cdot}}$ (1) 3) the similarity in mode of formation to a number of previously discovered pyrolysis reactions in our laboratory (3).

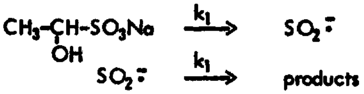
We had expected to find $SO_3^{\overline{\cdot}}$ radical formed in the pyrolysis of the sodium bisulfite adduct of an aldehyde. The formation of $SO_2^{\overline{\cdot}}$ could be the result of a radical rearrangement in the lattice cage.



A similar cage reaction in solution has been suggested (4):



If the logarithm of the steady state amounts of free radicals is plotted against $^1/_T$, a straight line is obtained. An energy of activation of 22.4 kcal./mole was obtained from the slope of the line and corresponds to the difference in energy of activation of reactions 1 and 2:



$$\underset{\text{OH}}{\text{CH}_3\text{-CH}}\text{-SO}_3\text{Na} \xrightarrow{k_1} \text{SO}_2^{\overline{\cdot}}$$

$$\text{SO}_2^{\overline{\cdot}} \xrightarrow{k_1} \text{products}$$

It might be expected that the main contribution to Δ E_1 would be the energy required to break the sulfur carbon bond and that Δ E_2 would be small as is common for reactions of radicals. A plot of the initial slopes of $SO_2^{\overline{\cdot}}$ formation as a function of time vs. $^1/_T$ gave a similar value for the activation energy. Since $\left[\frac{d\,[SO_2^{\overline{\cdot}}]}{dt}\right]_{t=o} = k_1\,[CH_3\text{-}CH(OH)SO_3Na]$ a plot of the initial slope as a function of temperature should give Δ E_1. Because the value obtained from either plot is approximately the same we conclude ΔE_2 is small and the activation energy for $SO_2^{\overline{\cdot}}$ formation is approximately 20-25 kcal.

Table 1 lists other examples of sodium bisulfite adducts which undergo similar decompositions. In the case of biacetyl two radicals were observed, $SO_2^{\overline{\cdot}}$ and probably an organic radical. No significant polar effect is observed in the decomposition of the sodium bisulfite adducts of substituted benzaldehydes. If the mechanism of radical formation involved ionic dissociation and subsequent electron transfer or if a significant portion of the decomposition was partitioning through an ionic decomposition pathway polar substituents like methoxy and chloro should influence the overall rate of radical formation. The fact that no large polar effect is observed lends support to a homolytic bond cleavage mechanism.

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Table I

$SO_2^{\overline{\cdot}}$ FORMATION IN THE PYROLYSIS OF SODIUM BISULFITE ADDUCTS

	Temperature	Amount
acetaldehyde	room temperature – 140°	+++
acetone	80-160°	+
cyclohexanone	120-140°	++
biacetyl	110-130° (2 radicals)	++
di-isopropylidene acetone (phorone)	120-140°	+
benzaldehyde	140°	++
anisaldehyde	140°	+
2,4-dichlorobenzaldehyde	160°	++
benzalacetone	80-130°	+