

THE THERMOLYSIS AND PHOTOLYSIS OF FERROCENYLSULPHONYL AZIDE.

EVIDENCE FOR A METAL-NITRENE COMPLEX IN THE THERMOLYSIS.


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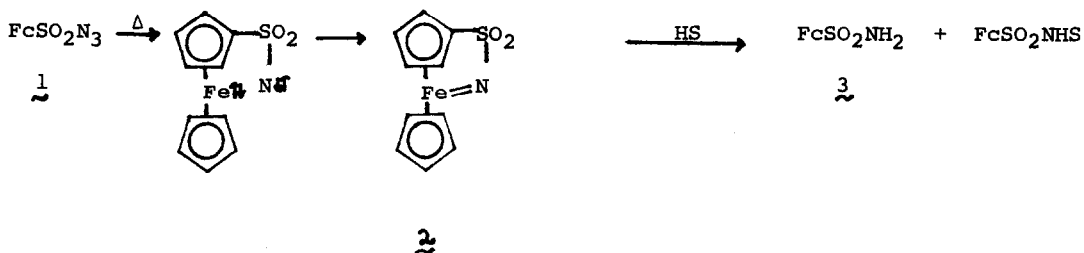
Though many studies have been carried out on sulphonyl nitrenes (1) little has been reported on the metal-catalyzed decomposition of sulphonyl azides. In view of the effort devoted to the stabilization of electron deficient intermediates by transition metals we have studied the decomposition of ferrocenylsulphonyl azide (1) and report our results which suggest that a metal-nitrene complex is involved in the thermolysis. The results of the thermal and photochemical decomposition of (1) in benzene, cyclohexene and cyclohexane are summarized in Table I.[‡] These

Table I. Thermal and photo-decomposition of ferrocenesulphonyl azide.% yield of products

| Solvent SH | Δ or $h\nu$ | FcSO ₂ NH ₂ | FcSO ₂ NHS | Fc-SO ₂ ^a NH | FcSO ₂ N  | FcH |
|--------------------------------|--------------------|-----------------------------------|-----------------------|---------------------------------------|---|-------|
| C ₆ H ₆ | Δ | 76.9 | 6.5 | - | - | 17 |
| | $h\nu$ | 14.3 | - | 67 | - | trace |
| C ₆ H ₁₂ | Δ | 48.3 | 24.0 | - | - | 20 |
| | $h\nu$ | 32.2 | - | 13.3 | - | 25 |
| C ₆ H ₁₀ | Δ | 85.5 | 8.0 | - | - | 2 |
| | $h\nu$ | 28.2 | - | 43.3 | 9.2 | trace |

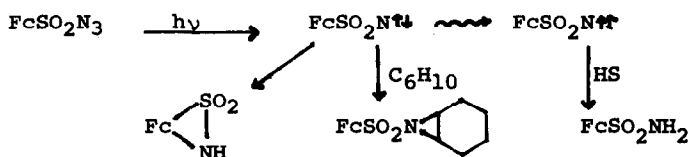
Fc = Ferrocenyl; FcSO₂NHS = insertion product where HS is solvent, $h\nu$ photochemical at 3500Å. ^a[2]-Ferrocenophane-1,1-dioxide.

results show that (1) decomposes via two competing pathways: N-N₂ cleavage to give nitrenes and S-N₃ cleavage to give ferrocene, probably derived from the ferrocenyl radical. Thermolysis gives much higher yields of ferrocene than does photolysis; S-N cleavage competes much more favourably with nitrene formation in the thermal process than it does in the photochemical process. The hydrogen abstraction product, FcSO₂NH₂ (3) is formed both in thermolysis and photolysis, and indeed is the main product of thermolysis. While hydrogen abstraction has been an important side-reaction of sulphonyl nitrenes (2), it becomes the main pathway in the copper-catalyzed decomposition of benzenesulphonyl azide, and it was suggested (3) that a copper-nitrene complex was involved. Likewise, a drastic increase in the yield of methanesulphonamide was observed when the corresponding azide was decomposed in an aromatic solvent in the presence of transition metal compounds (4). It thus appears that hydrogen abstraction is an important reaction of metal-nitrene complexes. A complex such as (2), formed by an interaction between the iron atom and the nitrene nitrogen, could account for the high yields of the sulphonamide in the thermal reactions (Scheme I). It is conceivable, however, that FcSO₂NHS could arise directly from the free singlet nitrene, a well-documented process (1).



Scheme I

There are several interesting features to the photochemical reaction. The intramolecular cyclization product, [2]-ferrocenophane-1,1-dioxide (5) is only obtained on photolysis but no intermolecular insertion products FcSO_2NHS are formed. Oxygen and hydroquinone are without effect on the yield of intramolecular cyclization product. The sulphonamide (3) formed in photolysis could arise from hydrogen abstraction by the triplet nitrene. Another product formed only on photolysis in cyclohexene is 7-ferrocenylsulphonyl-7-azabicyclo[4.1.0]heptane. The only other example of aziridine formation from a sulphonyl azide has been discussed by Kwart and Khan (3) as involving the attack of a copper-nitrene complex generated thermally on cyclohexene. Whether or not photolysis of a metal-nitrene complex is involved here is not known. Since the products from the thermalyses and photolyses are so different, however, we are tentatively formulating the photochemical reaction as shown in Scheme II.



Scheme II

Dimethylsulphoxide had a marked effect on both the thermal and the photochemical reaction, and there are no longer any significant differences between them. All the reactions, except for hydrogen abstraction, are suppressed and only a small amount of sulphoximine, $\text{FcSO}_2\text{N}=\overset{\text{O}}{\text{S}}\text{Me}_2$, is formed. The results are tabulated in Table II.

Table II. Effect of dimethylsulphoxide on product distribution (% yield)

| <u>Solvent</u> | <u>hν/Δ</u> | <u>FcSO₂NH₂</u> | <u>Sulphoximine</u> | <u>FcH</u> |
|--------------------------------------|--|---------------------------------------|---------------------|------------|
| DMSO | Δ | 40.6 | 0.6 | 2.6 |
| | h ν | 38.4 | 2.0 | 1.6 |
| C ₆ H ₆ /DMSO | Δ | 31.1 | - | trace |
| | h ν | 39.1 | 3.4 | trace |
| C ₆ H ₁₂ /DMSO | Δ | 17.0 | - | trace |
| C ₆ H ₁₀ /DMSO | h ν | 54.9 | - | trace |

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[‡] All new compounds have been fully characterized.

References

1. R. A. Abramovitch and R. G. Sutherland, Fortschr. Chem. Forsch., **16**, 1 (1970).
2. R. A. Abramovitch, C. I. Azogu and I. T. McMaster, J. Amer. Chem. Soc., **91**, 1219 (1969). R. A. Abramovitch, J. Roy, and V. Uma, Can. J. Chem., **43**, 3407 (1965).
3. H. Kwart and A. A. Kahn, J. Amer. Chem. Soc., **89**, 1950, 1951 (1967).
4. R. A. Abramovitch, G. N. Knaus, and V. Uma, J. Amer. Chem. Soc., **91**, 7532 (1969).
5. R. A. Abramovitch, C. I. Azogu, and R. G. Sutherland, Chem. Comm., 1439 (1969).