ratio of ammonia to thiocyanate aquation, that C* is the first excited quartet state rather than the doublet excited state. Direct photolysis gives a ratio of 22:1 on irradiation of the first ligand field band, and only 8:1 on irradiation in the region of the doublet band.[5]

In fact, pursuing an earlier suggestion,[5] it may be that the doublet state (^2E_g in O_h symmetry) undergoes only thiocyanate aquation, and the pure (nonvibrationally excited) first quartet excited state, only ammonia aquation. The ligand field excited quartet state produced in direct photolysis ($^4T_{2g}$ in O_h symmetry) is highly vibrationally excited and may more readily undergo intersystem crossing than does the pure state (see ref 9), thus accounting for the thiocyanate aquation component found in direct photolysis. In the sensitized reaction, however, energy transfer presumably occurs during the relatively long time scale of an encounter, and production of the pure excited state and hence only ammonia aquation might now be favored.

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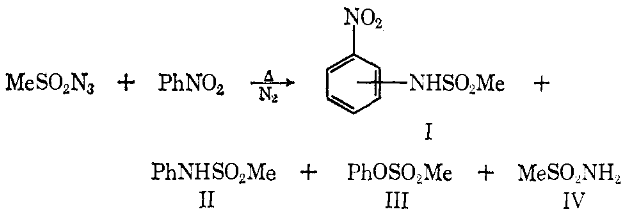
Aromatic Substitution by Sulfonyl Nitrenes. Singlet or Triplet Reactive Intermediates

Sir:

The reaction of methanesulfonyl nitrene, generated thermally from the azide, with benzene has been shown[1] to involve the addition of the singlet species to benzene (the same conclusion was reached for the reaction of carbethoxynitrene with benzene[2]) followed by ring opening of the aziridine intermediate and proton migration. The isomer ratios and reactivities in the reaction of $MeSO_2N$ with toluene, anisole, and chlorobenzene can be explained similarly, the rate-determining step being the addition step followed by a fast ring opening whose direction is determined by the nature of the substituent.[3] On this basis, it would be expected that an electron-attracting substituent would direct opening of the aziridine preferentially to that dipolar intermediate which would yield the *meta* isomer.

The proportion of this isomer did increase very markedly on going from toluene as substrate (2.4%) to benzonitrile (31.1%) and methyl benzoate (34.4%), but the *ortho* isomer still predominated: C_6H_5CN, *ortho*, 68.9; *meta*, 31.1; *para*, 0.0%; $C_6H_5CO_2Me$, *ortho*-, 64.3; *meta*, 34.4; *para*, 1.3%. The yields of anilides also dropped appreciably on going to C_6H_5CN (5.4%) and $C_6H_5CO_2Me$ (21.4%), but no product of addition to the substituent could be isolated. On going to nitrobenzene a dramatic change was observed. The results are summarized in Table I.



These results are entirely consistent with a rate-determining substitution by a highly electrophilic radical. The isomer ratio (degassed solvent) is similar to that observed in the homolytic *p*-nitrophenylation of nitrobenzene (*ortho*:*meta*:*para* 58:15:27).[4] The displacement of a nitro group by electrophilic radicals has been reported.[5] The effect of O_2 upon the yields of I and II is consistent with the interception of a triplet diradical by oxygen before it can react with nitrobenzene. The yield of III was not affected by O_2. In the presence of radicals, sulfonyl azides can undergo S–N bond cleavage.[8] The formation of III may then be rationalized as follows.

Table I. Reaction of $MeSO_2N_3$ with $PhNO_2$

Conditions	% products[a] I	II	III	IV
Degassed under N_2	5.3[b]	18.6	2.5	11.7
In air	2.8 (mainly *ortho*)	4.5	2.6	9.9
O_2 bubbled through	0.0	0.3	2.5	7.5

[a] In all cases much tar was formed. [b] *ortho*:*meta*:*para* 55.4:13.4:31.2.

$$MeSO_2N_3 + R\cdot \longrightarrow MeSO_2\cdot + RN_3$$

$$MeSO_2\cdot \xrightarrow{[O]} MeSO_3\cdot \xrightarrow{PhNO_2} MeSO_3Ph + [NO_2\cdot]$$

Oxygen abstraction by $MeSO_2\cdot$ either from nitrobenzene or possibly by disproportionation finds a parallel in the decomposition of $PhSO_2CHN_2$ in benzene when one of the products is $PhSO_3CH_2SO_2Ph$.[9]

Thus, the thermolysis of sulfonyl azides leads to singlet nitrenes which may add to surrounding aromatic molecules if the latter are sufficiently reactive to give aziridine intermediates. If the substrate is unreactive some of the singlet nitrenes may have time to drop to the triplet ground state[10] (alternatively, but less likely, the substituent could perhaps catalyze the singlet → triplet conversion), and the pattern of substitution then observed (with $PhCO_2Me$, PhCN, and $PhCF_3$) is consistent with an attack by a mixture of the two species, the singlet accounting for the marked increase in the proportion of *meta* isomer, but *ortho* still predominating because of the triplet contribution. With a sufficiently unreactive substrate ($PhNO_2$), complete conversion to

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the triplet state takes place before reaction with the aromatic nucleus.

Reactions were carried out between $MeSO_2N_3$ and methyl benzoate or benzotrifluoride in the presence of suitable additives in the hope of catalyzing the singlet → triplet conversion and then observing the pattern of substitution expected from the latter species. Some of the data are given in Table II.[11]

Table II. Methanesulfonamidation of Methyl Benzoate and Benzotrifluoride in the Presence of Various Additives

Conditions	% products *ortho*	*meta*	*para*	$MeSO_2$-NHC_6-H_4X	$MeSO_2$-NH_2
a. $PhCO_2Me$					
Sealed tubes under N_2	64.3	34.4	1.3	21.4	4.6
With oxygen	55.1	42.6	2.3	20.5	5.3
CCl_4 (40 molar excess)	62.9	35.0	2.1	12.9	*a*
CH_2Br_2 (40 molar excess)	29.9	57.5	12.6	1.1	44.2
Cobalt(III) acetylacetonate	32.3	63.3	4.4	2.2	*a*
Manganese(II) acetylacetonate	27.3	68.2	4.5	1.3	*a*
Manganese(II) acetylacetonate (trace)	61.4	37.1	1.5	16.6	*a*
$MnCl_2 \cdot 4H_2O$	61.6	36.7	1.67	13.6	*a*
Gattermann copper	56.2	40.5	3.3	5.8	*a*
Iron powder	60.7	37.9	1.4	19.1	*a*
b. $PhCF_3$					
Degassed under N_2	53.4	45.6	1.0	20.4	21.9
With oxygen	48.0	47.5	4.5	24.4	16.0
CH_2Br_2 (20 molar excess)	34.3	50.0	15.7	0.94	46.5
Copper(II) acetylacetonate	38.2	58.1	3.7	4.3	29.5
Manganese(II) acetylacetonate	43.9	54.1	2.0	4.1	29.0
$Co_2(CO)_8$	31.2	66.8	2.0	2.9	16.1
$Fe_3(CO)_{12}$	30.7	64.0	5.3	0.75	61.5
$Fe(CO)_5$	23.8	69.7	6.5	0.55	53.2

[a] Not determined.

Though there is considerable scatter of results among the different reaction conditions they appear to be generally consistent with a trapping by the additive (or side-tracking to an intermediate that abstracts hydrogen), efficient to varying degrees, of the triplet species present or formed, so that the pattern of substitution is more characteristic of an attack by a singlet species the more efficient the trapping becomes. With methylene bromide present in excess the main product was that of hydrogen abstraction (presumably by triplet nitrene) from CH_2Br_2 and the yield of substitution product dropped considerably. The proportion of *para* isomer formed was, exceptionally, also greater than in other cases, but the *meta* isomer predominated, as predicted on the basis of an addition by singlet nitrene. Carbon tetrachloride appeared ineffective. Transition metal compounds had a similar effect to CH_2Br_2, but to different extents depending on the nature of the addendum and its concentration. Manganous chloride, copper, and iron (all insoluble in the medium) had little, if any, influence upon the isomer ratio. The results are thus consistent with the intervention of both singlet and triplet sulfonyl nitrenes in these media.

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(11) All new compounds were adequately characterized.

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Intermolecular Energy Transfer and Sensitized Photolysis in the Biacetyl–Tetrachloroplatinate(II) System

Sir:

Sensitized photolysis has been a very useful tool for the analysis of the photochemical fates of organic molecules. Very recently, studies have begun to show that the technique can be extended to the study of inorganic complexes in solution. In 1968, Vogler and Adamson reported on the biacetyl–Co(III) ammine system,[1] and in 1969, Porter discussed the biacetyl–cobalticyanide system.[2] Other observations have demonstrated quenching of organic triplets by coordination compounds.[3–7]

We wish to report the results on the sensitized photoaquation of tetrachloroplatinum(II) complex. The observed absorption bands of $PtCl_4^{2-}$ at 330, 390, 470, and 550 mμ correspond to the transitions ${}^1A_{1g} \rightarrow {}^1E_g$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^3A_{2g}$, and ${}^1A_{1g} \rightarrow {}^3E_g$, respectively, in agreement with the assignment of Basch and Gray.[8] The high-energy triplet (${}^1A_{1g} \rightarrow {}^3B_{1g}$) reported[9] to occur at 417 mμ could not be observed since it is masked by the adjacent intense singlet (${}^1A_{1g} \rightarrow {}^1A_{2g}$) transition. The triplet transition (${}^1A_{1g} \rightarrow {}^3E_g$) was seen as a shoulder. It has not been observed in solution before.

The singlet transition of biacetyl occurs at 405 mμ, but is much less intense than the singlet transitions of $PtCl_4^{2-}$. Although the singlet–singlet transitions of biacetyl and $PtCl_4^{2-}$ overlap, it is possible to use a large excess of biacetyl and an almost negligible amount of the complex, such that most of the excitation energy is absorbed by biacetyl (donor).

A thoroughly degassed solution of 0.5 *M* biacetyl was excited with stimulating light from a 200-W xenon lamp and the emission spectrum recorded (Aminco-Bowman spectrofluorimeter) is given in Figure 1. Fluorescence occurs at 470 mμ and phosphorescence at 523 mμ with a ratio of 1:1.7. The phosphorescence of biacetyl is completely quenched in presence of 1×10^{-3} *M* $PtCl_4^{2-}$, while the fluorescence intensity remains essentially unchanged (Figure 1). Oxygen has a similar quenching effect on the phosphorescence of biacetyl and

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