

### Catalytic Effect of Ferric Ions on the Photoinitiated Autoxidation of Sulfite

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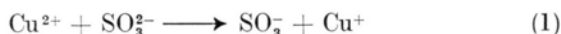
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Photoinitiation, Autoxidation, Sulfite,  
Sensitization, Ferric ions

The rate of the photoinitiated autoxidation of sulfite is considerably influenced by ferric ions in trace concentrations.

The autoxidation of sulfite, both thermal and photochemical, has long been considered to proceed by a free radical chain reaction where the  $\text{SO}_3^-$  radical acts as chain carrier<sup>1–4</sup>. In the thermal autoxidation of sulfite, which is one of the best known trace metal catalyzed reactions, the formation of the  $\text{SO}_3^-$  radical was explained by one-electron transfer between the catalyzing metal ions (*e.g.*  $\text{Cu}^{2+}$  ions) and the sulfite ions (equation (1)). In the photoinitiated reaction the formation of the radical by reaction (2) was assumed.



As has recently been shown<sup>5</sup>, reaction (1) cannot be one of the individual steps of the thermal reaction, due to high values of stability constants of sulfitecuprous complexes formed as intermediary products during the copper catalyzed autoxidation of sulfite. The reactive intermediates of the thermal reaction are probably ternary complexes of the type  $[\text{O}_2\text{Cu}(\text{SO}_3)_n]^{-2n+1}$ . The fact that all data on the autoxidation of sulfite suggested that both thermal and photoinitiated reactions proceed by the same mechanism made us investigate whether the course of the photochemical reaction was influenced by metal ions similarly as the course of the thermal reaction, and whether ternary complexes of the same type were also intermediates of the photochemical reaction.

The autoxidation of sulfite was carried out in a silica flow-cell irradiated by UV light. On one side the flow-cell was connected to a thermostated vessel bubbled with oxygen, on the other side it was

connected to a flow-cell of a spectrophotometer (Unicam SP 800). The circulating reaction mixture was irradiated with UV light emitted from a high pressure mercury spectral lamp of 90 W output (Philips No. 93136). The concentration of sulfite was followed spectrophotometrically at  $\lambda = 245 \text{ nm}$ .

The effect of the addition of various cations on the velocities of the thermal and photochemical reactions was followed, and it was found that the rate of the photoinitiated reaction was considerably influenced by ferric ions. Although cuprous ions catalyze the thermal reaction at trace quantities already, they exhibited no definite influence on the photochemical reaction. The catalytic effect of ferric ions is shown in Fig. 1.

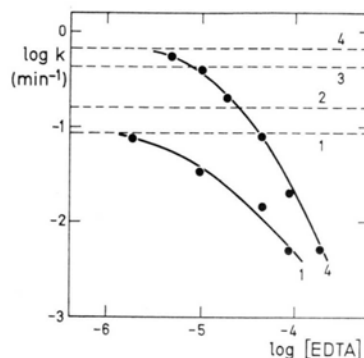


Fig. 1. Dependence of  $\log k$  on  $\log [\text{EDTA}]$  at various  $[\text{Fe}^{3+}]$ . Additions of  $[\text{Fe}^{3+}]$ : 1—0; 2— $1.9 \cdot 10^{-5} \text{ M}$ ; 3— $4.5 \cdot 10^{-5} \text{ M}$ ; 4— $9.1 \cdot 10^{-5} \text{ M}$   $k$  ( $\text{min}^{-1}$ );  $[\text{SO}_3^{2-}]_0 = 4.7 \cdot 10^{-5} \text{ M}$ ;  $[\text{O}_2] = 1.23 \cdot 10^{-3} \text{ M}$ ;  $25^\circ \text{C}$ .

The course of the photoinitiated autoxidation of sulfite follows the expression  $-\text{d}[\text{SO}_3^{2-}]/\text{d}t = k[\text{SO}_3^{2-}]$  (at  $[\text{O}_2] = \text{const.}$ ). The influence of ferric ions on the velocity constant is apparent from the plot  $\log k$  vs  $\log [\text{EDTA}]$  for various additions of ferric ions (Fig. 1). An increase in the concentration of ferric ions in the reaction system increases also the rate constant of the photoinitiated reaction (horizontal lines 1–4); addition of EDTA, on the contrary, brings the rate constant down (curves 1, 4). The same effect as with EDTA was found with some other chelating agents. Since chelating agents have a marked inhibiting influence at low concentrations already, the inhibiting effect cannot be explained by interaction with the assumed radical intermediates but only by binding catalytically active ferric ions into catalytically inactive complexes. Further experiments revealed that the photoinitiated autoxidation has, similarly to the thermal reaction, characteristic features of a trace metal catalyzed reaction: The value of the rate constant depends on the purity of the reaction system; the value of the rate constant decreases with decreasing level of trace metals and at the same time the experimental error of its determination increases.

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Comparing the individual values of the rate constants of a photoinitiated reaction obtained in reaction systems without additions of ferric ions at various [EDTA] it is apparent that the rate constant determined in a system without addition of the complexing agent is in fact the rate constant of a catalyzed reaction (Fig. 1, curve 1). The concentration of the catalyzing ions is determined by the purity of the system and by the "background" of the ferric ions (the catalytic influence of some other ions cannot be excluded). For this reason, it must be concluded that all literature data on the course of photoinitiated autoxidation of sulfite were obtained with undefined concentrations of catalytically active ions. The uncatalyzed photoinitiated reaction (if it does proceed) or catalyzed reactions in strictly defined conditions have so far not been studied.

The catalytic influence of ferric ions on the photoinitiated autoxidation of sulfite is evidently con-

nected with the existence of sulfiteferric complexes. These are known to have considerably high stability constants<sup>6,7</sup>, but no details have so far been reported on their photochemistry. The results presented in the present paper suggest that in the presence of oxygen and in UV light they exhibit behaviour as some other ferric complexes with reducing ligands<sup>8</sup>.

The formation of photochemically active ferric complexes is the cause of the well-known sensitizing effect of ferric ions on some reactions of molecular oxygen<sup>9</sup>. The results of the investigations of the photoinitiated autoxidation of sulfite, however, demonstrate that a marked sensitizing influence may be due to trace concentrations of ferric ions present in the system as impurities. In such a case, the information obtained by photochemical studies is distorted by the effect of trace metals and stands in the way to understanding the reaction mechanism.

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### Imidosulfonylhalogenide $(CF_3)_2C=N-S-X$ aus Thiazylhalogeniden und Bis(trifluormethyl)diazomethan

Imidosulfonylhalides  $(CF_3)_2C=N-S-X$  from  
Thiazylhalides and  
Bis(trifluoromethyl)diazomethane

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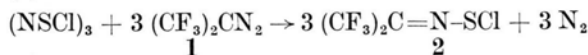
Trithiazyltrichloride, Thiazylfluoride,  
Bis(trifluoromethyl)diazomethane,  
Hexafluoro(isopropylidenimido)sulfonylchloride,  
Hexafluoro(isopropylidenimido)sulfonylfluoride

Imidosulfonylhalides  $(CF_3)_2C=N-SX$  ( $X =$   
Cl, F) are prepared from  $(CF_3)_2CN_2$  and  
 $(NSCl)_3$  and  $Hg(NSF_2)_2$ , respectively.

Während Trithiazyltrihalogenide  $(NSX)_3$  [ $X = Cl^1$ ,  
 $F^2$ ] und Tetrathiazyltetrahalogenide  $(NSX)_4$  [ $X = F^3$ ]  
seit einiger Zeit bekannt sind, konnte bisher nur das

Bis(trifluormethyl)nitroxid-Radikal,  $(CF_3)_2NO$ , als  
weiterer Ligand in diese Ringsysteme eingeführt  
werden<sup>4</sup>. Perhaloalkylderivate sollten ebenfalls  
stabil sein, eine geeignete Methode für ihre Dar-  
stellung erschien uns der Einschub von Carbenen in  
die S-X-Bindung.

Bei der Umsetzung von  $(NSCl)_3$  mit  $(CF_3)_2CN_2$ <sup>5</sup>  
bei 40 °C wird jedoch der Ring gespalten und unter  
Reduktion des Schwefels bildet sich in hoher Aus-  
beute Hexafluoro(isopropylidenimido)sulfonylchlorid  
(2):

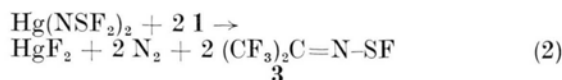


Die Chemie der Verbindung 2 ist ähnlich der der  
Perfluoroalkylsulfonylhalogenide<sup>6</sup>. Mit  $NH_3$  z. B. ent-  
steht aus 2  $(CF_3)_2CNSNH_2$ , aus diesem mit weiterem  
2  $[(CF_3)_2CNS]_3N$ , mit  $AgNCO$  das  
 $(CF_3)_2C=NSNCO$ <sup>7</sup>.

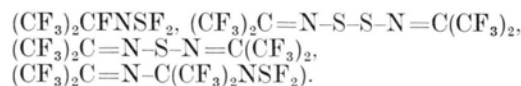
Die Darstellung des 2 entsprechenden Sulfonyl-  
fluorids gelingt nicht aus dem Chlorid; alle Ver-  
suche-, Cl gegen F auszutauschen, führten unter

Sonderdruckanforderungen an Prof. Dr. O. GLEMSER,  
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Oxidation des Schwefels zu  $(\text{CF}_3)_2\text{CFNSF}_2^8$ ,  $(\text{NSF})_3$  reagiert mit **1** erst oberhalb  $150^\circ\text{C}$  zu einem Gemisch schwer trennbarer C-N-S-F-enhaltender Substanzen, u.a. auch  $(\text{CF}_3)_2\text{CFNSF}_2$ . Mit  $\text{NSF}^3$  setzt sich **1** explosionsartig um, mit  $\text{Hg}(\text{NSF}_2)_2^9$  läßt sich ein Ablauf in der gewünschten Weise erreichen:



Während die bisher bekannten Stickstoff-Fluor-Schwefel(II)-Verbindungen, das Thiodifluoramin  $\text{CF}_3\text{SNF}_2^{10}$  und besonders die Dialkylaminosulfonylfluoride  $\text{R}_2\text{N}-\text{SF}$  ( $\text{R}=\text{CH}_3, \text{C}_2\text{H}_5$ )<sup>11</sup> so zersetzlich sind, daß eine vollständige Bestimmung ihrer Eigenschaften kaum möglich ist, scheinen die Perfluoralkylimidosulfonylfluoride stabil zu sein. **3** ist eine wasserklare Flüssigkeit, die bei  $55^\circ\text{C}$  unzersetzt destilliert und in Glasgefäßen bei Raumtemperatur über Wochen haltbar ist. Sie ist empfindlich gegen Oxidation (führt man die Reaktion (2) bei  $80^\circ\text{C}$  durch, so wird  $(\text{CF}_3)_2\text{CFNSF}_2$  isoliert), in der UV-Bestrahlung tritt Zersetzung ein (Bildung von



#### Arbeitsvorschrift

##### Hexafluorisopropylidenimidosulfonylchlorid (2)

6,20 g  $\text{S}_3\text{N}_3\text{Cl}_3$  (0,025 Mol) und 13,5 g  $(\text{CF}_3)_2\text{CN}_2$  (0,075 Mol) reagieren in einer Glasbombe bei  $40^\circ\text{C}$  innerhalb einer Woche zu 16,5 g **2**, Sdp.  $95^\circ\text{C}$  (95% Ausbeute). IR- und  $^{19}\text{F}$ -KMR-Spektren stimmen mit den Literaturdaten<sup>6</sup> überein (im KMR-Spektrum spalten die beiden CF-Signale bei  $0^\circ\text{C}$  in Quartetts auf,  $\delta_{\text{CF}_A} + 60,7$ ,  $\delta_{\text{CF}_B} + 69,2$  ppm,  $J_{\text{FF}} 6,5$  Hz).

##### Hexafluorisopropylidenimidosulfonylfluorid (3)

12,2 g  $\text{Hg}(\text{NSF}_2)_2$  (0,033 Mol) werden in eine 200 ml Glasbombe eingefüllt, eine halbe Stunde bei  $0^\circ\text{C}$  abgesaugt, danach 10,7 g (0,06 Mol)  $(\text{CF}_3)_2\text{CN}_2$  hinzukondensiert. Das Reaktionsgemisch wird aufgetaut und reagiert bei Raumtemperatur innerhalb von 24 Stunden\*. Das Produkt wird im Hochvakuum fraktioniert kondensiert ( $-80^\circ\text{C}$ ) und anschließend unter Normaldruck destilliert, Sdp.  $55^\circ\text{C}$ , Ausbeute 9,5 g (75%).

##### $\text{C}_3\text{F}_7\text{NS}$ (215,11)

Ber.	C 16,74	F 61,84	N 6,51	S 14,91,
Gef.	C 16,9	F 61,7	N 6,5	S 15,0.

##### IR (Gas):

1620 schw ( $\nu_{\text{C}=\text{N}}$ ), 1335 st, 1270 sst, 1186 ( $\nu_{\text{CF}}$ ), 985 st, 941 m, 745 schw, 713  $\text{cm}^{-1}$  st ( $\nu_{\text{S}-\text{F}}$ ).

##### $^{19}\text{F}$ -KMR:

Spektrum höherer Ordnung,  $\delta_{\text{SF}} + 71,5$ ,  $\delta_{\text{CF}_A} + 67,7$ ,  $\delta_{\text{CF}_B} + 66,1$  ppm (Intensitätsverhältnis 1:3:3).

##### Massenspektrum (rel. Int.):

215  $\text{M}^+$  (100), 196  $\text{M}-\text{F}^+$  (58), 177  $\text{M}-2\text{F}^+$  (10,5), (165  $\text{CF}_3\text{CFNSF}^+$  (4, 5)), 158  $\text{CF}_2\text{CFCNSF}^+$  (1, 7), 150  $(\text{CF}_3)_2\text{C}^+$  (7, 2), 146  $\text{M}-\text{CF}_3^+$  (55), (144  $\text{CF}_2\text{CFCSF}^+$ ? (11)), 131  $\text{CF}_3\text{CF}_2\text{C}^+$  (5, 5), 127  $\text{CF}_3\text{CNS}^+$  (9, 5), 108  $\text{CF}_2\text{CNS}$  (12), (101  $\text{CF}_3\text{S}^+$ ? (33)), 100  $\text{CF}_3\text{CF}^+$  (9, 5), 96  $\text{CF}_2\text{NS}^+$  (5, 5), 93  $\text{CF}_3\text{CC}^+$  (2, 8), 82  $\text{CF}_2\text{S}^+$  (10), 81  $\text{CF}_3\text{C}^+$  (2, 2), 76  $\text{CF}_2-\text{CN}^+$  (44, 5), 69  $\text{CF}_3$  (67), 64  $\text{CF}_2\text{N}^+$  (7, 5), 63  $\text{CFS}^+$  (4, 5), 58  $\text{CNS}^+$  (4), 51  $\text{SF}^+$  (53), 50  $\text{CF}^+$  (19, 5), 46  $\text{NS}^+$  (31), 45  $\text{CFN}^+$  (4), 44  $\text{CS}^+$  (11, 5), 32  $\text{S}^+$  (18), 31  $\text{CF}^+$  (15, 5).

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\* Auch bei dieser Arbeitsweise traten mehrere heftige Explosionen ein.

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