

THE N-BROMOSUCCINIMIDE-SUCCINIMIDE ANION COMPLEX,
AN INTERMEDIATE IN THE ELECTRON TRANSFER MEDIATED
REDUCTION OF N-BROMOSUCCINIMIDE BY SUCCINIMIDE ANION

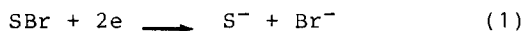
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Abstract: Complexes between N-bromosuccinimides and succinimide anions are shown to be intermediates in the reduction of N-bromosuccinimides, and a method for their synthesis as tetra-n-butylammonium salts is described.

The electrochemical reduction of N-bromosuccinimide (SBr) in acetonitrile (AN) generates the succinimidyl radical (S·) by the reactions shown below:



The n-value for this overall process is 1, and the intermediacy of the succinimide anion (S⁻) was demonstrated by trapping the anion with alkylating agents to give N-alkylsuccinimides.¹

Reaction (2) was also studied in a purely chemical system with S⁻ added as a quaternary ammonium succinimide. Measurements of the rate of this reaction indicated that it was not a simple, second-order reaction between SBr and S⁻, but that it involved the prior, rapid formation of a complex (C), between SBr and S⁻, which then underwent electron-transfer in a rate-determining step to form S·, as indicated in (3) and (4).

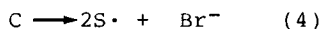


TABLE I
IMIDE - IMIDE SALT COMPLEXES

Imide	Tetra-N-Butyl- ammonium Salt of	% Yield	MP °C	ANALYSES									
				Calcd.			Found						
				C	H	N	Br	I	C	H	N	Br	I
N-Bromosuccinimide	Succinimide	92	78-79d	55.59	8.55	8.10	15.41		55.30	8.53	7.90	15.60	
N-Bromosuccinimide	Phthalimide	84	83-88d			7.42	14.10				7.19	13.70	
N-Iodosuccinimide	Succinimide	91	99-100d	50.97	7.84	7.43		22.44	50.22	7.59	7.32		22.40
N-Iodosuccinimide	Tetramethyl- succinimide	72	98-104d			6.76		20.41			6.63		20.27
N-Iodosuccinimide	Maleimide	93	105-107d	51.15	7.51	7.46		22.52	50.99	7.73	7.44		22.31
N-Iodosuccinimide	Phthalimide	86	95-105d			6.85		20.68			6.72		20.90
N-Iodosuccinimide	Diacetamide	25	100-102d			7.40					7.26		
N-Bromotetramethyl- succinimide	Tetramethyl- succinimide	77	166-168d	60.94	9.59	6.66	12.67		60.83	9.47	6.65	12.34	
Phthalimide	Phthalimide	65	83-88d			7.84					7.45		

We now wish to report that the complex, C, which has hitherto been only a postulated entity required to explain the rate measurements, has been prepared, that it is stable in the solid state for a limited period of time (2-3 weeks at room temperature) and that its properties and reactions are consistent with the reaction mechanism previously proposed.¹ Such complexes are relatively general, and this report will describe complexes formed from imide anions and both N-halosubstituted imides and imides unsubstituted on nitrogen.

The following preparation of the complex from SBr and tetra-n-butylammonium succinimide (TBAS) is typical. Ether (150 ml.) was added to a solution of SBr (0.88g; 0.00494 mole) in AN (10 ml.). A solution of 0.988M TBAS in AN (5 ml.) and then ether (50 ml.) were added. On cooling in the freezer the product crystallized; yield 2.36g. (92%); m.p. 78-79° d. The additional complexes that were prepared are assembled in Table 1, which includes the analytical results supporting the assigned empirical formulae.

Not surprisingly, a solution of the above complex in AN is completely equivalent to a solution of equivalent quantities of SBr and TBAS in AN. This is attested to by the complete correspondence of the IR spectra, the cyclic voltammetry tracings and measurements of the rates of appearance of succinimide, as followed by the increase in the intensity of the NH band at 3280 cm^{-1} , for the two solutions. These results are consistent with the hypothesis that the complex is an intermediate in the reduction of SBr, but they do not provide completely unambiguous proof.

However, definite proof is provided by results obtained in the reduction of N-bromotetramethylsuccinimide (TMSBr).² The electrochemical reduction of TMSBr at 25° in AN at Pt at -0.8V vs. Ag/Ag⁺ (0.1M), with tetra-n-butylammonium fluoborate (TBAF) as the supporting electrolyte, shows

an n-value of 0.95F/mole. As in the case of SBr, the anion (TMS^-) is an intermediate in this process, and it can be captured by methyl tosylate. Thus, when 0.0998M TMSBr is electrochemically reduced in the presence of 0.5M methyl tosylate the n-value increases to 1.84F/mole and an 88% yield of N-methyltetramethylsuccinimide is produced. In the absence of the methyl tosylate no products attributable to the tetramethylsuccinimidyl radical ($\text{TMS}\cdot$), e.g., tetramethylsuccinimide, are obtained. At 25° the only product of the electrochemical reduction is the TMSBr- TMS^- complex, obtained in essentially quantitative yield as the tetra-n-butylammonium salt. This is the complex described in the next to last entry in Table 1, and its identity with the electrochemical reduction product is indicated by the fact that the synthetic complex and TBAF in AN at the appropriate concentrations has an IR spectrum over the range 4000-1000 cm^{-1} that is identical to the final electrolyzed solution. At 25° in AN no electron transfer takes place with this complex, but at reflux temperature the electron transfer does occur, the $\text{TMS}\cdot$ radical forms, and tetramethylsuccinimide is obtained.

References

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2. R. E. Pearson and J. C. Martin, J. Amer. Chem. Soc., (1963) 85, 3142.

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