TABLE I

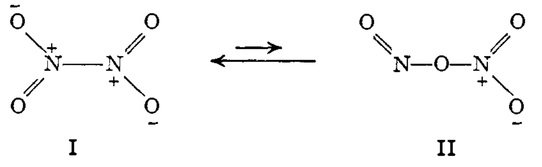
$$XH \text{ or } XNa + N_2O_4 \begin{cases} \xrightarrow{a} XNO + (H \text{ or } Na)NO_3 \\ \xrightarrow{b} XNO_2 + (H \text{ or } Na)NO_2 \end{cases}$$

Run	Reactant	Temp., °C.	Solvent	Yields,[a] % Path a		Path b	
1	$(C_2H_5)_2NH$	0	CH_2Cl_2	$(C_2H_5)NNO$ (98)[93],	$(C_2H_5)_2NH_2{}^+NO_3{}^-$ (95)	$(C_2H_5)_2NNO_2$ (0),	$(C_2H_5)_2NH_2{}^+NO_2{}^-$(3)
2	$(C_2H_5)_2NH$	−80	CH_2Cl_2	(0)	(0)	(97)[93]	(100)
3	$(C_2H_5)_2NH$	−80	Ether	(39)	(40)	(59)	(59)
4	n-$C_4H_9O^-Na^+$	0	$CH_2Cl_2 + C_4H_9OH$	C_4H_9ONO (99)	$NaNO_3$ (97)	$C_4H_9ONO_2$ ..	$NaNO_2$ (1)
5	n-$C_4H_9O^-Na^+$	−80	$CH_2Cl_2 + C_4H_9OH$	(6)	(5)	(89)	(93)
6	n-$C_4H_9O^-Na^+$	−50	$CH_2Cl_2 + C_4H_9OH$	(51)	(52)	..	(48)
7	n-$C_4H_9O^-Na^+$	−80	CH_2Cl_2[b]	(26)	(37)	(56)	(56)
8	$C_6H_5CH_2CH_2OH$[c]	−80	CH_2Cl_2[b]	RONO (93)	HNO_3 (100)	$RONO_2$ (0)	HNO_2 (7)
9	n-$C_6H_{13}NH_2$	−80	CH_2Cl_2[b]	$C_6H_{13}OH$[d] ..	$C_6H_{13}NH_3{}^+NO_3{}^-$ (35)	$C_6H_{13}NHNO_2$ [53]	$C_6H_{13}NH_3{}^+NO_2$ (55)
10	$CH_3CON^-CH_3Na^+$	−80	CCl_4[b]	$CH_3CON(NO)CH_3$ (98)	$NaNO_3$ (100)	..	$NaNO_2{}^-$(0)

[a] Values in brackets refer to yields of isolated products. Values in parentheses were determined as follows: column 1, ultraviolet; column 2, see footnote 2; column 3, infrared; column 4, see footnote 3. [b] Heterogeneous runs (others homogeneous throughout run). [c] Allowed to stand for 24 hr. at −80° to complete the reaction. All others worked up as soon as reactants were mixed. [d] $C_6H_{13}ONO_2$ (6%) also was obtained.

temperature and the volatiles were removed under vacuum. Nitrate ion was determined in the residue by means of the nitron reagent[2] and nitrite ion was determined by the method of Stempel.[3] The organic products in the volatile fractions were determined spectrophotometrically (infrared and ultraviolet). Each organic product also was isolated and identified by a comparison of its properties and spectra with those of authentic samples.

The N_2O_4 reactions are unusually sensitive to conditions as illustrated by the effect of temperature (runs 1 and 2; 4, 5, and 6), the effect of base strength (runs 2 and 8, 8 and 5), the effect of solvent (runs 2 and 3), and the effect of heterogeneity (runs 5 and 7, 10). Previous to our work, it had been reported that ammonia,[4a] primary aromatic amines,[4b] and alcohols[4c] were nitrosated by N_2O_4. In no case was nitration observed.[5] Most of the chemical reactions of N_2O_4, therefore, involve nitrosation; nitration (as the primary reaction) occurs only at low temperatures, and then only with reactants that are strong bases. We interpret our results in terms of an equilibrium between I, the predominant form of nitrogen tetroxide,[6]



I II

and an isomeric form II.[7] The nucleophilic displacement of nitrite ion from I leads to nitration and the displacement of nitrate ion from II leads to nitrosation.[8]

We wish to thank the Research Corporation for its support of part of this work.

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(4) (a) F. Falk and R. N. Pease, THIS JOURNAL, **76**, 4746 (1954); (b) B. Houston and T. B. Johnson, *ibid.*, **47**, 3011 (1925); (c) A. D. Yoffe and P. Gray, *J. Chem. Soc.*, 1412 (1951). For reaction with other organic compounds, see J. L. Riebsomer, *Chem. Rev.*, **36**, 157 (1945).

(5) Riebsomer (footnote 4) has listed a number of cases where partial nitration was observed in other reactions of N_2O_4 (especially those at high temperatures where oxidation reactions occur).

(6) Structure I was assigned to crystalline N_2O_4 by J. S. Broadley and J. M. Robertson (*Nature*, **164**, 915 (1949)) and to gaseous N_2O_4 by O. W. Smith and K. Hedberg (*J. Chem. Phys.*, **25**, 1282 (1956)).

(7) The unsymmetrical form (II) has been invoked by a number of investigators to account for the nitrosations observed with N_2O_4, *e.g.*, F. Seel, *Z. anorg. Chem.*, **261**, 75 (1950).

(8) Similar reactions have been proposed by H. Taube and M. Anbar (THIS JOURNAL, **77**, 2993 (1955)) for the hydrolysis of N_2O_4.

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INITIATION OF STYRENE POLYMERIZATION AT A CATHODE

Sir:

Polymerization of styrene initiated by electrons has been observed when the monomer is exposed to the electric discharge of a Tesla coil,[1] β-irradiation,[2,3] and to cathode rays from a generator of the resonant transformer type.[4] Polymerization of styrene initiated by electrons supplied by the colored anion obtained by reaction of an aromatic hydrocarbon, such as naphthalene, with metallic sodium in a suitable solvent has also been noted.[5]

During the course of studies of reduction of organic compounds in anhydrous pyridine solution by unipositive magnesium anodically generated a novel and potentially valuable phenomenon was encountered, namely, the polymerization of styrene initiated by electrons supplied at a cathode. With styrene as additive, sodium iodide as electrolyte, and magnesium electrodes, electrolyses carried out at 30° for about 45 hr., in a divided cell[6] gave no

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(1) K. Otozai, S. Kume, S. Nagai, T. Yamamoto and S. Fukushima, *Bull. Chem. Soc. Japan*, **27**, 476 (1954).

(2) W. H. Seitzer, R. H. Goeckermann and A. V. Tobolsky, THIS JOURNAL, **75**, 755 (1953).

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(5) (a) N. D. Scott, U. S. Patent 2,181,771 (1939); (b) M. Szwarc, M. Levy and R. Milkovich, THIS JOURNAL, **78**, 2656 (1956); (c) M. Szwarc and A. Rembaum, *J. Polymer Sci.*, **22**, 189 (1956); (d) D. E. Paul, D. Lipkin and S. I. Weissman, THIS JOURNAL, **78**, 116 (1956).

(6) M. D. Rausch, W. E. McEwen and J. Kleinberg, THIS JOURNAL, **76**, 3622 (1954).

evidence for the formation of a reduction product in the anolyte, and the magnesium appeared to enter solution in its normal dipositive state. However, investigation of the catholyte upon completion of electrolysis revealed the presence of a polymer.

The catholyte, following an electrolysis at a current density of approximately 0.004 amp. per sq. cm., was treated with ice water, neutralized with 6 *M* hydrochloric acid, and the resulting white precipitate was collected by filtration and dried. The solid was dissolved in benzene, the solution filtered and the filtrate evaporated, leaving a glassy, brittle residue. *Anal.* calcd. for $(C_8H_8)x$: C, 92.27; H, 7.73. Found: C, 92.31; H, 7.78. The molecular weight was determined to be about 1800 by the viscosity method.[7] The solid material obtained from the catholyte after an electrolysis carried out at a current density of 0.0007 amp. per sq. cm. (*Anal.* Found: C, 92.07; H, 7.88) had a molecular weight of approximately 2800.[8] Control experiments revealed that styrene subjected to the conditions cited above, except for the electrolysis, could be recovered unchanged.

Conclusive proof that the polymerization was initiated by electrons supplied by the cathode and not by sodium metal plated out during electrolysis has been obtained. In one experiment, electrolysis was carried out in the usual manner but in the absence of styrene. The latter substance was then added, the mixture permitted to stand for 46 hr., and the polymer which formed (buff in color) was isolated as described above. *Anal.* Found: C, 90.94; H, 7.89; N, 0.94; mol. wt., 1600. In a second experiment, metallic sodium was added to a solution of styrene and sodium iodide in pyridine and the mixture was allowed to stand for 43 hr. at 30°. The polymer which was produced was also buff colored. *Anal.* Found: C, 90.06; H, 7.75; N, 1.07; mol. wt., 1500. Calculation of molecular weights from nitrogen analyses gave results in substantial agreement with those from viscosity measurements. The presence of nitrogen in the polymers formed in the reactions with sodium strongly suggests that the effective initiating agent in these cases is an anion formed by transfer of an electron from sodium to pyridine. Initiation of polymerization of styrene by anions has been observed previously.[9] The absence of nitrogen in the polymers obtained from electrolyses would appear to eliminate definitely from further consideration the possibility of an anion-catalyzed polymerization.

The only other report of initiation of polymerization at a cathode is that of Parravano,[10] who found that the efficiency of polymerization of methyl methacrylate in aqueous solution depended on the hydrogen overvoltage as well as on the current density. However, the evidence indicated that polymerization was initiated by atomic hydrogen deposited at the cathode rather than by electrons.

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RECEIVED SEPTEMBER 30, 1957

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[7] A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

[8] Neither polymer contained any nitrogen, as shown by direct determination.

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[10] G. Parravano, THIS JOURNAL, **73**, 628 (1951).

BIOSYNTHESIS OF CERAMIDE BY RAT BRAIN HOMOGENATES[1]

Sirs:

The formation of sphingosine *in vivo* has been investigated in this laboratory[2] and elsewhere.[3] Recently, Brady and co-workers have reported the incorporation of labeled serine by a dialyzed supernatant solution of rat brain into a sphingosine fraction obtained by acid hydrolysis of a lipid extract.[4] The conversion of radioactive serine to ceramide (N-acylsphingosine) by rat brain homogenates has now been demonstrated. When 3-C^{14} DL-serine was added to a sucrose homogenate obtained from the brain of 15–20 day old rats and the mixture was incubated with triphosphopyridine nucleotide, adenosine triphosphate, nicotinamide, magnesium, pyridoxal phosphate, tris buffer, and palmityl coenzyme A (Table I), labeled ceramide was formed.

Ceramide was isolated by stopping the reaction with trichloracetic acid and extracting the residue with 2:1 chloroform–methanol. The lipid mixture was passed through a column containing Florisil, Dowex 2 and Dowex 50 in order to remove ionic lipids.[5] The solvent was removed and the neutral lipids were taken up in chloroform and added to a column of silicic acid which was developed with increasing concentrations of methanol in chloro-

TABLE I

FORMATION OF CERAMIDE

Each tube contained 100 μM. Tris buffer, *p*H 7.5, 30 μM. $MgSO_4$, 40 μM. nicotinamide, 5 μM. ATP, 1 μM. TPN, 1 λM. Palmityl CoA, 5 μM. 3-C^{14} DL-serine 500,000 c./min./μM., and 1 ml. of enzyme obtained after centrifuging a 20% homogenate in 0.25 *M* sucrose and 0.001 *M* Versene for 10 minutes at 600 g. ATP was omitted in Expt. 2. 1 μM. DPN, 1 μM. CoA, 5 μM. DL-O-P-serine, 2 μM. sphingosine, and 5μM. n-palmiylserine were added as indicated. Each tube in Expt. 4 contained 1 mg. of Tween 20. The final volume was 2 ml. and incubations were carried out at 37° for 1 hr.

Expt.	Additions	Total counts/min.
1	Complete	490
	Complete, zero time	15
	No TPN	385
	DPN, no TPN	460
	P-Serine instead of serine	165
2	Complete	665
	CoA, no Palmityl-CoA	295
3	Complete	1100
	+ N-Palmitylserine	850
4	Complete	1055
	+ Sphingosine	590

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[1] Supported by a grant from the U. S. Public Health Service.

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