T. G. Ermakova, A. I. Gritsa,
N. M. Deriglazov, L. A. Tatarova,
V. V. Keiko, T. I. Vakul'skaya,
and V. A. Lopyrev

The polarographic reduction of 1-substituted 1,2,4-triazoles in dimethylformamide (DMF) and acetonitrile was studied. 1-Methyl-, 1-ethyl-, and 1,2,4-triazoles are not reduced on a mercury electrode over the range of potentials accessible for polarography. 1-Phenyl-1,2,4-triazole and 1-vinyl-1,2,4-triazole are reduced in acetonitrile via a one-electron mechanism at high negative potentials. The reduction of 1-vinyl-1,2,4-triazole is accompanied by polymerization of the electrolysis products. A possible mechanism for the electrochemical reduction is discussed.

1-Viny1-1,2,4-triazole is a promising monomer for the creation of polymers that have a set of valuable technical properties [1, 2]. The increased requirements for the quality of polymers are in turn responsible for the vigorous search for the most effective methods for polymerization, particularly electrochemical methods. However, the literature contains information that indicates that in the case of electrochemical initiation N-vinylimidazole undergoes polymerization with ring opening [3]. We therefore attempted to examine the behavior of 1-viny1-1,2,4-triazole under conditions of electrochemical reduction on a dropping mercury electrode. To obtain more nearly complete information regarding the reduction of vinyltriazole, wealso investigated 1-alky1- and 1-pheny1-1,2,4-triazoles.

Like the starting 1,2,4-triazole [4, 5], triazoles Ia and Ib are not reduced on a dropping mercury electrode.



Fig. 1. Polarograms of the reduction of phenyltriazole Id (1, 2) and vinyl-triazole Ic (3, 4) in DMF (1, 3) and acetonitrile (2, 4).

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 408-410, March, 1980. Original article submitted August 1, 1978; revision submitted July 31, 1979.

313

UDC 547.792:543.253

One one-electron wave  $[E_{1/2} = -2.47 \text{ V}$  in acetonitrile, and  $E_{1/2} = -2.35 \text{ V}$  in dimethylformamide (DMF), Fig. 1] appears on the polarograms of phenyltriazole Id. The addition of a proton donor — phenol or water — shifts the wave  $\sim 0.1 \text{ V}$  to the positive region with a simultaneous twofold increase in its height. The steepness of the wave also increases, and this constitutes evidence for the transfer of two electrons. Since neither benzene [6], nor triazole I are electrochemically reduced, the reduction of phenyltriazole Id can be explained by an increase in the conjugation chain, due to interaction of the  $\pi$ electrons of the phenyl ring with the aromatic system of the triazole ring.

One's attention is drawn to the fact that the  $E_{1/2}$  value of phenyltriazole and the  $E_{1/2}$  value of chlorobenzene [6] are close to one another. This is in agreement with the literature data on the similar electronic effects of a 1-H-1,2,4-azolyl substituent and halogens [7,8] ( $\sigma_p = 0.365 \pm 0.04$  for the 1,2,4-triazol-1-yl substituent [6], and  $\sigma_p = 0.25$  for halogens [9]). On the basis of the Kauffmann principle [7] and from the available literature data on the reduction of halobenzenes [10] one can propose the following scheme for the reduction of phenyltriazole Id. The first and determining step of the process is transfer of one electron to the depolarizer molecule:



The resulting anion radical undergoes rapid decomposition with splitting out of a 1,2,4triazole anion and an aryl radical, which is reduced much more readily than the starting compound:



In the presence of proton donors (phenol and water) the final reduction products will be triazole I and benzene. In fact, triazole I was identified in the reaction medium by the method of reference spots in thin-layer chromatography (TLC).

In contrast to phenyltriazole Id, vinyltriazole Ic is reduced in a more remote negative region, and the character of the reduction is determined by the solvent used. One one-electron wave is observed in acetonitrile  $(E_{1/2} = -2.72 \text{ V})$ ; this is confirmed by comparison with the polarogram of nitrobenzene recorded under identical conditions and also by calculations with the Ilkovic equation. A two-electron wave  $(E_{1/2} = -2.57 \text{ V})$  is observed immediately in DMF, which itself may serve as a source of protons [11]. No changes are observed on the polarogram when a proton donor (phenol) is present.

Ethyltriazole Ib, along with a small amount of triazole I and poly(1-viny1-1,2,4-triazole), was isolated as the principal product of the reduction of vinyltriazole Ic in DMF with chromatographic separation of the products of preparative electrolysis. The formation of a polymer in the cathode space occurs due to polymerization of vinyltriazole Ic under

IC + 2e; 2H+ --- 1b

the influence of the radicals or anion radicals that are formed during the reduction. It should be noted that, according to the data from IR spectroscopy, the triazole rings remain unchanged in the polymer obtained in the polarographic reduction of vinyltriazole Ic, whereas polymerization with ring opening occurs in the case of electrochemical initiation of the polymerization of vinylimidazole [3].

## **EXPERIMENTAL**

The polarographic reduction was carried out with an OH-102 polarograph (Hungary) with a dropping mercury electrode (m = 2.0 mg/sec, t = 3.5 sec) at 20°C. The depolarizer concentration was  $10^{-3}$  mole/liter. The solvents used for this research were purified by known methods [12, 13]. The purity of the solvents and the base electrolyte, viz., tetra-n-butylammonium perchlorate, was verified by polarography.

Compounds Ia-d were obtained by the methods in [1, 14-16] and were purified by repeated vacuum distillation. The degree of purity (99.95%) was estimated by gas-liquid chromatography (GLC) (the columns used were a 2 m×3 mm column filled with 10% Lukopren G-1000 and a 3 m×3 mm column filled with 10% XE-60; the analysis was carried out with temperature programming from 80 to 200°C).

The reduction products were separated by preparative gas chromatography with a 1.2 m× 10 mm column filled with 15% DS-550 polydimethylsiloxane liquid on Chromaton at 120°C and were identified by reference spots in TLC [on Silufol UV-254 with chloroform ethanol (9:1) and acetone-methanol-acetic acid-water (75:20:5:4)] and IR spectroscopy.

## LITERATURE CITED

- L. P. Makhno, T. G. Ermakova, E. S. Domnina, L. A. Tatarova, G. G. Skvortsova, and V. A. Lopyrev, USSR Inventor's Certificate No. 464584 (1974); Byul. Izobr., No. 11, 66 (1975).
- 2. H. Hopff and M. Lippay, Makromol. Chem., <u>66</u>, 157 (1963).
- 3. A. Z. Trifonov, I. Schopov, D. J. Kolev, and Y. Tsenov, Compt. Rend. Acad. Bulg. Sci., 28, 767 (1975).
- 4. Yu. P. Kitaev, I. M. Skrebkova, and L. I. Maslova, Izv. Akad. Nauk SSSR, No. 10, 2194 (1970).
- 5. Yu. P. Kitaev, I. M. Skrebkova, V. V. Zverev, and L. I. Maslova, Izv. Akad. Nauk SSSR, No. 1, 28 (1971).
- 6. C. K. Mann (ed.) and K. Barnes, Electrochemical Reactions in Nonaqueous Systems, Dekker (1970).
- 7. T. Kauffmann, Angew. Chem. Int. Ed., No. 10, 743 (1971).
- 8. P. Bonchet, C. Congelet, and I. Elegnero, J. Chem. Soc., Perkin Trans., 5, 449 (1974).
- 9. H. Hine, Physical Organic Chemistry, McGraw-Hill, New York (1962), p. 87.
- 10. S. G. Mairanovskii, Ya. P. Stradyn', and V. D. Bezuglyi, Polarography in Organic Chemistry [in Russian], Khimiya, Leningrad (1975), p. 160.
- V. D. Bezuglyi, Polarography in the Chemistry and Technology of Polymers [in Russian], Khimiya, Leningrad (1968), p. 44.
- 12. S. Wawronek and M. E. Runner, J. Electrochem. Soc., 99, 457 (1952).
- 13. P. H. Rieger, J. Bernal, W. H. Reinmut, and G. K. Fraenkel, J. Am. Chem. Soc., <u>85</u>, 683 (1963).
- 14. M. R. Alkinson and I. B. Polva, J. Chem. Soc., 141 (1954).
- 15. G. Pellizari and A. Soldi, Gazz. Chim. Ital., <u>35</u>, 373 (1905).
- 16. E. G. Kovalev and I. Ya. Postovskii, Khim. Geterotsikl. Soedin., No. 4, 740 (1968).