INVESTIGATION OF THE REVERSIBLE CONDENSATION OF CHLOROACETALDEHYDE WITH NITRO-COMPOUNDS

M. Kh. Akhmetov, V. M. Belikov,
Yu. N. Belokon', R. A. Sadykov,
and S. S. Novikov

UDC 542.953+547.446.1+547.414

As was shown earlier, the reversible addition of nitro-compounds to aldehydes is a convenient model reaction for investigating problems associated both with the basicity of carbanions with respect to carbon [1-5] and with the acidity of a number of aldehydes with respect to carbanions [5]

$$\mathrm{RA} + \mathrm{OH}^{\ominus} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{ROH} + \mathrm{A}^{\ominus} \qquad (1)$$

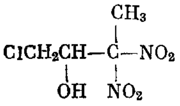
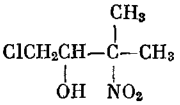
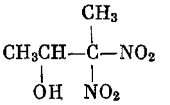
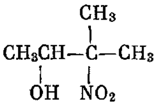
Ra represents a nitroalcohol; $A^{\ominus}$ is the carbanion of a nitro-compound; ROH is the hydrated form of the aldehyde.

We had earlier suggested that the weakness and strength of acids and bases are a consequence not only of the electronic effects of substituents in the molecules of these compounds, but also to a substantial degree of the steric interaction between the reacting acids and bases [5]. The interaction of chloroacetaldehyde with nitro-compounds is interesting from this standpoint. We should expect that chloroacetaldehyde will be a stronger acid than, for example, acetaldehyde, on account of the inductive effect of chlorine [6]. For this reason, the equilibrium (1) for chloroacetaldehyde should be shifted to the left in comparison with acetaldehyde. The increase in the size of the radical R as we go from acetaldehyde to chloroacetaldehyde should lead to the same effect, which is equivalent to an increase in the strength of the acid. However, the inductive and steric effects of chlorine should exert mutually compensating effects on the decomposition of γ-chloro-β-nitroalcohols. On the one hand, we should expect a certain deceleration of the rate of decomposition on account of the inductive effect of chlorine [7]; on the other hand, an increase in the volume of the group in the γ-position (for CH_3, $E_S = 0$; for $ClCH_2$, $E_S = -0.24$ [8]) should lead to an increase in the rate of decomposition on account of an increase in the steric stress in the initial state of the nitroalcohol (a close analogy to this can be found in the increase in the rate of decomposition of Mannich bases as a result of steric factors [9]). The correspondence of the theoretically expected results to the observed results in a study of the reversible reaction of chloroacetaldehyde with nitro-compounds should answer the question of how correct our concepts of the interaction of steric and polar effects in the reversible reaction with aldehydes and carbanions are.

This work was devoted to an investigation of 1-chloro-3,3-dinitrobutanol-2 (I) and 1-chloro-3-nitro-3-methylbutanol-2 (II). The study of the position of equilibrium (1) for (II) and the rate of decomposition of (II) at high pH of the medium is complicated by the hydrolysis of chlorine in chloroacetaldehyde [10]. Therefore, for (II) we determined only the observed rate of decomposition under the action of hydroxyl ions. The data obtained are summarized in Table 1, which presents for comparison data characterizing the decomposition of nitroalcohols formed by the condensation of acetaldehyde with dinitroethane and 2-nitropropane [4]. As can be seen from the table data, the results obtained correspond to those expected. The rates of decomposition of the nitro-alcohols (I) and (III), (II), and (IV) are practically identical within the limits of the experimental error. The rates of formation (k_{-1}) of the alcohols (I) and (III) are also close. This is undoubtedly a consequence of the mutual compensation of the steric and inductive effects of chlorine in the decomposition and formation of compounds (I) and (II).

Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR; N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1649-1651, July, 1970. Original article submitted December 8, 1969.

TABLE 1. Kinetic Parameters of the Decomposition and Formation of a Number of Nitroalcohols in Water at 25° and Ionic Strength 0.5

Nitroalcohol		k_1, $mole^{-1} \cdot sec^{-1}$	k_{-1}, $mole^{-1} \cdot sec^{-1}$	Kequil	k_1', $mole^{-1} \cdot sec^{-1}$*
 $ClCH_2CH(OH)-C(CH_3)(NO_2)-NO_2$	(I)	$(1,44 \pm 0,38) \cdot 10^7$	0,025	$(5,7 \pm 3,3) \cdot 10^8$ †	$0,95 \pm 0,5$
 $ClCH_2CH(OH)-C(CH_3)(NO_2)-CH_3$	(II)	$(1,22 \pm 0,03) \cdot 10^2$			
 $CH_3CH(OH)-C(CH_3)(NO_2)-NO_2$	(III)	$8,9 \cdot 10^6$		$3,7 \cdot 10^7$	0,48
 $CH_3CH(OH)-C(CH_3)(NO_2)-CH_3$	(IV)	$1,33 \cdot 10^2$			

---

* The rate constant of the interaction of the carbanion of the nitro-compound with the aldehyde after a consideration of the degree of its hydration.

† It can be assumed with sufficient reliability that chloroacetaldehyde is almost entirely hydrated under the experimental conditions [11], $K_d = [ClCH_2CHO]/[ClCH_2CH(OH)_2] = 0.27$.

At the same time, the constant of the equilibrium (1) for (I) is greater than for (III). Precisely this effect should be expected on the basis of concepts of the increase in the rigidity of the C-acid when electronegative substituents are introduced into its molecule.

EXPERIMENTAL

Chemically pure reagents were used. The water was redistilled twice before use, the second time in a stream of nitrogen. The purity of dinitroethane and 2-nitropropane was verified gas chromatographically on a "Pye" instrument, with neopentyl glycol adipate as the stationary phase. Gas – liquid chromatographic analysis indicates the presence of impurities in these nitro-compounds, not exceeding 5% of the total amount of the compound in 2-dinitroethane and in 2-dinitropropane.

1-Chloro-3-nitro-3-methylbutanol-2. This was produced according to the same procedure [12] as the production of (IV), with a yield of 20%; bp 126-128° (16 mm); n_D^{20} 1.4730. Found: C 36.29, 36.41; H 5.97, 5.99%. $C_5H_{10}NO_3Cl$. Calculated: C 35.81; H 6.01%. IR spectrum (in a thin layer): 1545, 1350 cm^{-1} (nitro-group), 3470 cm^{-1} (hydroxy group).

1-Chloro-3,3-dinitrobutanol-2. This was produced according to the procedure for the production of (III) in [13] with a yield of 80%; bp 87° (1 mm); n_D^{20} 1.4850. Found: C 24.43, 24.14; H 3.91, 3.82; Cl 17.45, 17.41%. $C_4H_7N_2O_5Cl$. Calculated: C 24.18; H 3.53; Cl 17.88%. IR spectrum (in a thin layer): 1580, 1325 cm^{-1} (nitro-group), 3500 cm^{-1} (hydroxy group).

The kinetics of the decomposition of (I) and (II) was studied spectrophotometrically according to the increase in the optical density in the region of the absorption maxima of the anions of 2-nitropropane and dinitroethane [4, 13]. The decomposition of (I) was studied in acetate buffer solutions at pH 3.90-4.45. The decomposition of (II) was studied in borate buffer solutions at pH 8.70-9.65. The number of measurements was equal to six for (II) and (I). The kinetic curves of the decomposition of (I) and (II) obey the principles of first-order kinetics. The data obtained are summarized in Table 1.

The equilibrium of the decomposition of (I) into the starting materials was studied spectrophotometrically in an acetate buffer solution at pH 3.90 according to the procedure of [2]. The value obtained was an average of five measurements.

CONCLUSIONS

1. The decomposition of 1-chloro-3,3-dinitrobutanol-2 and 1-chloro-3-nitro-3-methylbutanol-2 in water at 25° with an ionic strength of 0.5 was studied.

2. The equilibrium constant of the dissociation of 1-chloro-3,3-dinitrobutanol-2 in water at 25° was found.

LITERATURE CITED

1. J. Hine and R. Weimer, J. Amer. Chem. Soc., 87, 3387 (1965).
2. T. N. Hall, J. Organ. Chem., 29, 3587 (1964).
3. V. M. Belikov, Yu. N. Belokon', N. G. Faleev, and Ts. B. Korchemnaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1477 (1967).
4. V. M. Belikov, Yu. N. Belokon', N. S. Martinkova, and N. G. Faleev, Izv. Akad. Nauk SSSR, Ser. Khim., 2130 (1969).
5. V. M. Belikov, Yu. N. Belokon', N. S. Martinkova, and N. G. Faleev, Izv. Akad. Nauk SSSR, Ser. Khim., 2136 (1969).
6. R. G. Pearson and J. Songstad, J. Amer. Chem. Soc., 89, 1827 (1967).
7. V. M. Belikov, V. N. Leibzon, and L. M. Kozlov, Izv. Akad. Nauk SSSR, Ser. Khim., 322 (1970).
8. Steric Effects in Organic Chemistry [Russian translation], IL (1960), p. 599.
9. M. M. Dolgaya, Yu. N. Belokon', and V. M. Belikov, Izv. Akad. Nauk SSSR, Ser. Khim., 14 (1969).
10. R. Bell, in: New Problems of Physical Organic Chemistry [Russian translation], Mir (1969), p. 245.
11. R. Bell, in: New Problems of Physical Organic Chemistry [Russian translation], Mir (1969), p. 240.
12. D. Nightingale and J. Janes, J. Amer. Chem. Soc., 66, 352 (1944).
13. Yu. N. Belokon' and V. M. Belikov, Izv. Akad. Nauk SSSR, Ser. Khim., 528 (1967).