FREE-RADICAL ADDITION OF N-ETHYLACETAMIDE TO UNSATURATED COMPOUNDS

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Abstract

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FREE-RADICAL ADDITION OF N-ETHYLACETAMIDE TO UNSATURATED COMPOUNDS

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Free organic radicals in reactions with unsaturated compounds exhibit electron-donor, electroneutral, or electron-acceptor properties, but a clear classification of them according to this feature does not yet exist. This is explained by the fact that, unlike heterolytic reagents, free radicals do not possess a clearly pronounced electrophilic or nucleophilic character. Indeed, many organic compounds can add by a radical mechanism, although at different rates, to multiple bonds both with increased and with decreased electron density.

It is known that electron-attracting atoms or groups directly bonded to the atom on which the unpaired electron is localized increase the degree of electrophilicity of the radical (for example, it increases in the series $CH_3\cdot < Cl_3C\cdot < F_3C\cdot$ (1)). The nucleophilic properties of free radicals in addition reactions at multiple bonds have not been specially studied by anyone.

In 1961 Friedman and Schechter carried out the addition of N-methylacetamide to octene-1 in the presence of tert-butyl peroxide (2). The reaction proceeds through the stage of homolysis of the C—H bond in the methyl group adjacent to the nitrogen atom and leads to the formation of N-nonylacetamide.

We studied, under standard conditions, the radical addition reaction of $CH_3CONHCH_2CH_3$ at the multiple bond of heptene-1, allyl alcohol, methacrylate, and dimethyl maleate, and came to the conclusion that the radical $CH_3CONH\dot{C}HCH_3$, formed from N-ethylacetamide at the initiation or chain-transfer stage, possesses a nucleophilic character. Indeed, the electrophilicity of the C=C bond in the indicated series of unsaturated compounds increases from heptene-1 to dimethyl maleate, and in the same series the yield of the resulting 1 : 1 adducts increases. Probably the nucleophilicity of the radical $CH_3CONH\dot{C}HCH_3$ is a consequence of the appearance of an effective negative charge on the carbon atom bearing the unpaired electron, owing to the shift toward it of the electron density of the unshared pair of nitrogen.

In the reaction

Fig. 1. Infrared spectrum of the methyl ester of N-acetyl-β-carbomethoxy-γ-aminovaleric acid

Figure 1: Fig. 1. Infrared spectrum of the methyl ester of N-acetyl-β-carbomethoxy-γ-aminovaleric acid

$$CH_3CONH-\dot{C}H-CH_3 + CH_2{=}CH-C_5H_{11} \rightarrow$$
$$CH_3CONHCHCH_2\dot{C}HC_5H_{11} - CH_3CONHCHCH_2CH_2C_5H_{11}$$
$$\begin{array}{cc} | & | \\ CH_3 \quad \text{A} & CH_3 \quad \text{B} \end{array}$$

the polar effect exerts a retarding influence on the course of the process, which is manifested in the low yield of the 1 : 1 adduct. Conversely, in the reaction

$$CH_3CONH-\dot{C}H-CH_3 + HC-COOCH_3 \quad \begin{array}{c} || \\ HC-COOCH_3 \end{array} \rightarrow CH_3CONH-\overset{+}{C}H \quad \begin{array}{c} | \\ CH_3 \end{array} \quad \dot{C}H-\overset{-}{C}HCOOCH_3 \quad \begin{array}{c} | \\ COOCH_3 \end{array}$$
$$\text{V}$$
$$\rightarrow CH_3CONHCH-\dot{C}HCHCOOCH_3 \rightarrow CH_3CONHCH-CHCH_2COOCH_3$$
$$\begin{array}{cc} | & | \\ CH_3 & COOCH_3 \end{array} \qquad \begin{array}{cc} | & | \\ CH_3 & COOCH_3 \end{array}$$
$$\text{G} \qquad\qquad \text{D}$$

the intermediate state of which, apparently, can to a considerable extent be represented by the contribution of the ionic structure (B); the polar effect promotes the addition step by lowering its activation energy. The increased stability of the carbomethoxy-conjugated radical in comparison with radical A also facilitates its formation. However, we believe that the polar effect has a stronger influence than the stabilizing one. Otherwise, one would expect a decrease in the yield of the 1 : 1 adduct on going from methyl acrylate to dimethyl maleate, since here the steric influence of two carbomethoxy groups, hindering the reaction, becomes apparent

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of two carbomethoxy groups (the stabilizing effect in the radical $CH_3CONHCH(CH_3)CH_2\dot{C}HCOOCH_3$ and in radical is approximately the same). In reality the yield not only does not decrease, but even increases somewhat.

In order to judge more reliably the correctness of the conclusion drawn, two series of experiments were carried out—at the ratio N-ethylacetamide : unsaturated compound : tert-butyl peroxide of 10 : 1 : 0.1 and 30 : 1 : 0.1. The results obtained agree well. The experimental conditions, yields of the 1 : 1 adducts, their structure, and the amount of the higher-boiling products obtained ("residue") are given in Table 1. From the figures presented in Table 1 it is evident that heptene-1 and allyl alcohol form 1 : 1 adducts with N-ethylacetamide in yields approximately 2 times lower (30-45%) than methyl acrylate and dimethyl maleate (70-87%). The percentage content of residue in the reaction products of the latter two unsaturated compounds is considerably smaller than that of the first two.

Identification of the 1 : 1 adducts presents no difficulty, with the exception of methyl N-acetyl-β-carbomethoxy-γ-aminovalerate ( )—the product of the interaction of $CH_3CONHCH_2CH_3$ with dimethyl maleate. In the molecule of this substance there are two asymmetric carbon atoms; consequently, it must exist as a mixture of two racemic diastereoisomers. The racemates have different melting points, but it is rather difficult to separate them. An infrared spectrum (Fig. 1) was obtained for a mixture of the two racemates on a UR-10 spectrograph in the regions 400-700 (KBr prism), 700-2000 (NaCl prism), and 2800-360 [[unclear: range endpoint as printed]] (LiF prism) cm^{-1}. The spectrum corresponds to structure ; it contains bands characteristic of an amide of the type $RNHCOR^1$—1570 (disappearing in CCl_4 solution), 1690, 3090, 3275 cm^{-1}, as well as a band at 1746 cm^{-1} for the stretching vibrations of the C = O group of esters ([3]).

We thank L. D. Lubuzh for carrying out the spectral analysis.

Experimental Part

Procedure for experiments I-VIII. N-Ethylacetamide, taken in an amount of 90% of the calculated value (the calculated amount is indicated in Table 1), was placed in a flask of volume 0.5 l and heated to 155–160°. Over the course of 6 h, with stirring, a solution of the unsaturated compound was added uniformly to the flask

Table 1

Experiment No.	N-Ethylacetamide A	Unsaturated compound B	A, mol	B, mol	Peroxide, mol	T-re, °C	Duration, h	Yield of 1 : 1 adduct, g	Yield of 1 : 1 adduct, %	Residue, g	Residue, %
I	$CH_3CONHC_2H_5$	$CH_2=CH-C_5H_{11}$	0.3	0.03	154–158	6	18.4	33	17	48	

Experiment No.	N-Ethylacetamide A	Unsaturated compound B	A, mol	B, mol	Peroxide, mol	T-re, °C	Duration, h	Yield of 1 : 1 adduct, g	Yield of 1 : 1 adduct, %	Residue, g	Residue, %
II	$CH_3CONHC_2H_5$	$CH_2=CH(CH_2)_3CH_3$	0.1	0.01	0.01	154—157	6	8	43	4.3	35
III	$CH_3CONHC_2H_5$	$CH_2=CH(CH_2)_2CH_3$	0.1	0.03	0.03	154—158	6	13	30	13	50
IV	$CH_3CONHC_2H_5$	$CH_2=CHCH_2OH$	0.1	0.009	0.009	154—156	6	5.8	45	4.2	42
V	$CH_3CONHC_2H_5$	$CH_2=CHCOOCH_3$	0.3	0.03	0.03	155—160	6	36.5	70	13	26.5
VI	$CH_3CONHC_2H_5$	$CH_2=CHCOOCH_3$	0.1	0.01	0.01	154—157	6	13.4	77	3	18
VII	$CH_3CONHC_2H_5$	$CH_3OOCCH=CHCOOCH_3$	0.3	0.03	0.03	154—158	6	60.5	87	9	13
VIII	$CH_3CONHC_2H_5$	$CH_3OOCCH=CHCOOCH_3$	0.1	0.01	0.01	154—157	6	20	86	3.5	12

···compound and tert-butyl peroxide in the remaining amount (10%) of N-ethylacetamide. After the addition of the solution was completed, the reaction mixture was kept at 155—160° for one more hour, after which it was distilled in vacuum. In experiments I and II, during distillation, 7 g (0.07 mole) and 3 g (0.03 mole), respectively, of unreacted heptene-1 were isolated; in the other experiments the presence of unsaturated compounds in the reaction mixture was not observed. The weight of the high-boiling "residue" was determined after separation of the 1 : 1 adduct from the reaction mixture. The properties of the adducts obtained are given below.

Experiment I. N-Acetyl-2-aminoheptane. B.p. 103—104° (0.5 mm), n_D^{20} for the supercooled liquid 1.4500. M.p. of crystals purified by sublimation, 35.5—36°.

Found, %: C 70.68, 70.67; H 12.82, 12.62
$C_{11}H_{24}NO$. Calculated, %: C 71.29; H 12.51

Experiment III. N-Acetyl-4-aminopentanol-1. B.p. 131—132° (0.5 mm), n_D^{20} 1.4720; d_4^{20} 1.0203; MR found 39.85, calculated 39.69.

Found, %: C 58.41, 57.90; H 10.36, 10.26
$C_7H_{15}NO_2$. Calculated, %: C 57.90; H 10.41

Experiment V. Methyl ester of N-acetyl-γ-aminovaleric acid. B.p. 108–109° (0.5 mm), n_D^{20} 1.4582; d_4^{20} 1.0564; MR found 44.54, calculated 44.56.

Found, %: C 55.32, 55.32; H 8.86, 8.75
$C_8H_{15}NO_3$. Calculated, %: C 55.47; H 8.72

Experiment VII. Methyl ester of N-acetyl-β-carbomethoxy-γ-aminovaleric acid. B.p. 132–137° (0.5 mm); m.p. 96–100° (from ether–heptane solution).

Found, %: C 52.07, 51.94; H 7.35, 7.31
$C_{10}H_{17}NO_5$. Calculated, %: C 51.93; H 7.41

Dihydrazide–m.p. 221.5–222.5°.

Found, %: C 41.32, 41.24; H 7.50, 7.54; N 30.45, 30.22
$C_8H_{17}N_5O_3$. Calculated, %: C 41.55; H 7.41; N 30.29

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Note: Figure translations are in progress. See original paper for figures.