RADIATION-CHEMICAL SYNTHESIS OF AMINO ACIDS FROM A MIXTURE OF CO_2, NH_3, AND CH_4 IN THE PRESENCE OF SILICA GEL

N. T. Kartel' and V. V. Strelko

UDC 541.15

The radiation-chemical synthesis of complex organic compounds is acquiring ever-increasing importance because a number of reactions, which would not occur under normal conditions, can be successfully conducted in a radiation environment [1]. At the same time, the yield of radiation-chemical specific products is small in the majority of cases. It would be interesting, therefore, to study radiation synthesis processes in the presence of adsorbents (silica gel in particular), because the realization of these reactions on the surface layers (in the adsorbed state) is expected to alter the selectivity of the process and, therefore, lead to an increase in the radiation-chemical yields, at least in certain reactions. Furthermore, it is well known [2, 3] that irradiated adsorbents can actually absorb radiation energy and transform it into the layer of adsorbed molecules. Irradiated silica gels generate greater quantities of hydrogen atoms and surface radicals [4-6] in the reaction zone, which also causes an intensification of the process. Finally, the probability of transformations occurring in the surface layers should be greater than in a homogeneous medium due to the absorptive concentration of substances (an increase in the number of collisions) and to the possible catalytic effect of the surface on the recombination processes of radicals and ions [7].

Taking into account all the above, we attempted to conduct the radiation-chemical synthesis of amino acids in a multicomponent system comprising a mixture of CH_4, NH_3, CO_2, and finely-porous silica gel (S_{sp} = 600 m^2/g) with a varying $\geq$Si—OH group content in the surface layers.* The gas mixture (50 μmole of each component) was exposed to γ rays (1-200 Mrad dosage) at room temperature in sealed ampoules containing various quantities of pre-evacuated silica gel. After irradiation the ampoules were opened and the silica gel treated with a 5 N HCl solution.† The amino acid content in this solution was analyzed using electrophoresis, paper chromatography, and the AAA-881 amino acid analyzer.

The results of completed experiments indicate that the presence of silica gel exhibits a substantial effect on amino acid synthesis. In control specimens without silica gel, the amino acid yield was so small that it was beyond the limit of sensitivity for the methods of analysis employed. The yield increased as the amount of sorbent was augmented, reaching a threshold at a ratio of 150 μmole gas mixture (50 μmole of each component) per gram of silica gel. The change in the degree of dehydration on the silica gel surface also affects the sensitivity of individual amino acid synthesis (see Table 1), and the total yield exhibits symbatic variability with respect to the content of surface $\geq$Si—OH groups, i.e., the suppliers of active hydrogen atoms to the radiation field [4-6] (Fig. 1). The important role of hydrogen atoms which are emitted from the surface is also demonstrated by the fact that substitution of —OH group protons by Ca^{2+} ions

*The synthesis of amino acids from a mixture comprising the simplest gases under the action of a high-frequency discharge and ionizing radiation was studied earlier in connection with the origin of prebiological systems [8].

†Special experiments determined that this treatment ensures the complete elimination of amino acids from the silica gel.

L. V. Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Teoreticheskaya i Éksperimental'naya Khimiya, No. 4, pp. 556-558, July-August, 1974. Original article submitted August 7, 1973.

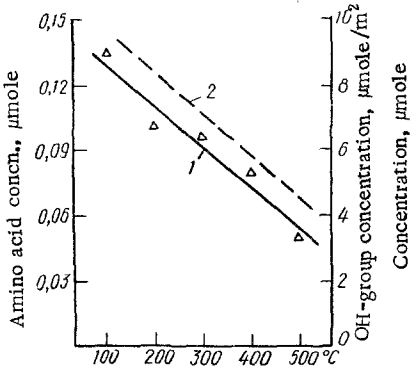

Fig. 1

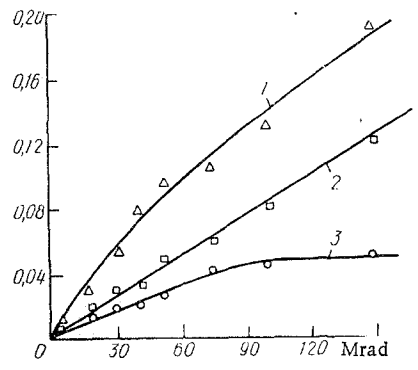

Fig. 2

Fig. 1. Amino acid yield (1) and —OH group content in the surface layers (2) [9] versus the evacuation temperature of the silica gel.

Fig. 2. Synthesized amino acid concentration as a function of the absorbed γ-radiation dosage: 1) total amino acid concentration produced during radiation-chemical analysis; 2) glycine; 3) alanine.

TABLE 1. Amino Acid Yield (μmole) after γ Irradiation (50 Mrad dosage) of a Mixture Comprising CH_4, NH_3, and CO_2 (150 μmole) on Ordinary and Ca Silica Gel (0.8 g), Evacuated at Various Temperatures

Amino acid	100° C		200° C		300° C		400° C		500° C	
	SG	Ca-SG	SG	Ca-SG	SG	Ca-SG	SG	Ca-SG	SG	Ca-SG
Glycine	0,031	—	0,054	0,003	0,047	0,011	0,020	0,032	0,028	0,035
Alanine	0,019	—	0,032	—	0,037	0,001	0,052	0,011	0,017	0,014
Valine	0,009	—	0,003	—	—	—	0,029	—	—	—
Leucine	0,006	—	—	—	—	—	—	—	—	—
Isoleucine	0,006	—	—	—	—	—	—	—	—	—
Phenylalanine	0,007	—	—	—	—	—	—	—	—	—
Serine	0,008	—	—	—	—	—	—	—	0,002	—
Threonine	0,006	—	—	—	—	—	—	—	—	—
Asparagine	0,010	—	—	—	—	—	—	—	—	—
Glutamine	0,007	—	—	—	0,007	—	—	—	0,003	—
Tyrosine	0,008	—	—	—	0,003	—	—	—	—	—
Histidine	0,010	—	—	—	—	—	—	—	—	—
Lysine	0,010	—	—	—	0,004	—	—	—	—	—
Total amino acid yield	0,137	—	0,099	0,003	0,098	0,012	0,081	0,043	0,050	0,049

(on Ca silica gel) (see Table 1) causes the synthesis to proceed much more slowly.

We also studied the accumulation of amino acids (at the optimum gas mixture/sorbent ratio) as a function of the absorbed dosage. It is evident from Fig. 2 that the total amino acid yield increases with an increase in dosage of up to ~150 Mrad; the nature of the accumulation of individual amino acid types is apparently different in each case (see curves 2 and 3).

In summary, the obtained data indicate that the efficiency of the radiation-chemical synthesis of amino acids from a mixture comprising the simplest gases is significantly increased in the presence of silica gel, and the nature of the process is dependent upon the state of the sorbent surface.

LITERATURE CITED

1. I. V. Vereshchinskii, Khim. Vys. Énerg., 4, 483 (1970).
2. G. M. Zhabrova and V. I. Vladimirova, Usp. Khim., 38, 711 (1969).
3. Ya. S. Pshezhetskii, A. G. Kotov, V. K. Milinchuk, V. A. Roginskii, and V. M. Tupikov, EPR of Free Radiation Chemistry [in Russian], Khimiya, Moscow (1972), p. 428.

4. V. V. Strelko and K. A. Suprunenko, Teor. i Éksp. Khim., 2, 694 (1966).
5. K. A. Suprunenko, V. V. Strelko, and A. M. Kabakchi, Teor. i Éksp. Khim., 5, 353 (1969).
6. K. A. Suprunenko, V. V. Strelko, D. I. Shvets, and A. M. Kabakchi, Adsorption and Adsorbents [in Russian], No. 1, Naukova Dumka, Kiev (1972), p. 112.
7. R. Kekelbergs, A. Kruk, and A. Frene, Catalysis. New Physical Methods of Investigation [Russian translation], Mir, Moscow (1964).
8. A. I. Oparin (editor), The Origin of Prebiological Systems [Russian translation], Mir, Moscow (1969), p. 342.
9. L. Little, Infrared Spectra of Adsorbed Species, Academic Press (1967).