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ELECTRON AND γ-RAY INDUCED ADDITION OF FORMAMIDE TO OLEFINS

Joshua Rokach(1) and Carl Heinrich Krauch
Max-Planck-Institut für Kohlenforschung, Abt. Strahlenchemie,
Mülheim-Ruhr, Germany

Dov Elad
Organic Chemistry Department, The Weizmann Institute of
Science, Rehovoth, Israel

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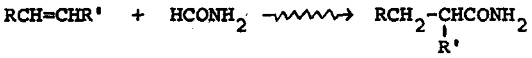
Synthetic applications of ionizing radiation have so far been limited, and only few cases are reported in the literature2). In an effort to study the synthetic potentialities in this field we investigated series of R-H type addition reactions to double bonds. Examples of such additions have appeared recently in the literature. Alcohols3), aldehydes4), halogenated hydrocarbons5) and chlorosilanes6) have been found to add to olefins to yield the corresponding 1:1 adduct.

We have found that formamide adds to olefins by electron and γ-ray induced reaction. By adjusting the experimental conditions we were successful in obtaining the 1:1 adducts in yields up to 80 %. It seems worthwhile mentioning that the reaction proceeds cleanly and it is an easy matter to separate the main product. In this respect the reaction seems to have some advantages as compared to the thermal[7] and the photochemical counterpart[8]. In the latter case the necessity in the use of sensitizers for higher chemical yield leads sometimes to undesirable by-products. The general reaction can be pictured as follows:



$$RCH{=}CHR' + HCONH_2 \rightsquigarrow RCH_2-\underset{R'}{CH}CONH_2$$

A typical experiment can be described in the following way: A mixture of 1-octene (2g), formamide (25cc), t-butanol (25cc, to homogenize the reaction mixture) was irradiated at room temperature, for 70 hours at a dose rate of $9.1\cdot10^{5}\cdot cc^{-1}\cdot rad\cdot hr^{-1}$. The reaction mixture was then normally worked up, as described in[7], to yield 1.5 g nonanamide, (53 %). The following table contains a list of the olefins used, products, chemical yields and G values.

TABLE

olefin[9]	product	yield %	G value
1-heptene	n-octanamide	62	3
1-octene	n-nonanamide	53	3
1-decene	n-undecanamide	60	3.5
1-dodecene	n-tridecanamide	50	3
cyclohexene	cyclohexanecarboxamide	50	3.5
cyclooctene-cis	cyclooctanecarboxamide	78	3
cyclodecene-cis	cyclodecanecarboxamide	58	3
cyclodecene-trans	cyclodecanecarboxamide	62	3.2
cyclododecene	cyclododecanecarboxamide	51	3
norbornene	*exo*-norbornanecarboxamide	80	2.5

In connection with the table the following should be pointed out:

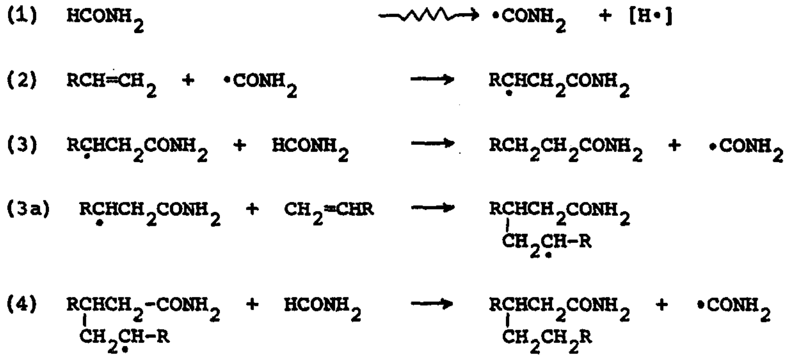
a - Most of the reactions yielded comparable results with electron and γ-irradiation.

b - The γ-ray source was 5000 c ^{60}Co [10]. The electron source was a 2 MeV G.E. resonance transformer. Used dose: 10^8 rad/hr.

c - The G values are calculated from the ^{60}Co experiments. The use of greater quantities of olefins in the reaction mixture leads to a rise in the G values.

d - Yields are calculated on the olefin employed. Conversion at the used dose is not quantitative. It is estimated that the unreacted olefin is in the range of 15 to 20 %.

It seems that the chain radical mechanism proved for the photochemical reaction is also valid in this case. The steps can be formulated as follows:



(1) $HCONH_2 \rightsquigarrow \cdot CONH_2 + [H\cdot]$

(2) $RCH{=}CH_2 + \cdot CONH_2 \longrightarrow R\underset{\bullet}{C}HCH_2CONH_2$

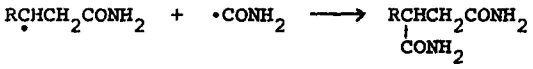
(3) $R\underset{\bullet}{C}HCH_2CONH_2 + HCONH_2 \longrightarrow RCH_2CH_2CONH_2 + \cdot CONH_2$

(3a) $R\underset{\bullet}{C}HCH_2CONH_2 + CH_2{=}CHR \longrightarrow \begin{array}{l}RCHCH_2CONH_2\\ \;|\\ CH_2\underset{\bullet}{C}H-R\end{array}$

(4) $\begin{array}{l}RCHCH_2-CONH_2\\ \;|\\ CH_2\underset{\bullet}{C}H-R\end{array} + HCONH_2 \longrightarrow \begin{array}{l}RCHCH_2CONH_2\\ \;|\\ CH_2CH_2R\end{array} + \cdot CONH_2$

Steps 3a and 4 are proved by the isolation of 2:1 as well as higher telomers from the reaction mixture.

Evidence for the existence of the carbamoyl radical is obtained by the following facts: In the electron accelerator experiments, oxamide and alkylsuccinamides were isolated. Due to higher L.E.T., the concentration of the carbamoyl radicals is higher in this case than with the ^{60}Co source experiments, in which those by-products could not be detected. Oxamide presumably results from the dimerisation of the $\cdot CONH_2$ radical, and the alkylsuccinamides formation can be explained by a termination step of the following type:



$$R\underset{\bullet}{C}HCH_2CONH_2 + \cdot CONH_2 \longrightarrow R\underset{CONH_2}{\underset{|}{C}}HCH_2CONH_2$$

It is interesting to compare these results with the photochemical ones$^{8)}$. In sunlight the U.V intensity being low, these compounds are not formed whereas irradiation with mercury high pressure 80 watts lamp, oxamide and alkylsuccinamides are formed. Concerning the production of the $\cdot CONH_2$ radical from the formamide, it seems possible that direct and indirect processes may be operative. The direct process may involve a) ionisation, of the formamide followed by a breakdown to $\cdot CONH_2$ radicals, and b) excitation of formamide to one or more different electronic states and dissociation of the excited molecule to $H\cdot$ and $\cdot CONH_2$ radicals. The indirect process may involve the abstraction of hydrogen from formamide by some radical or solvated electron in the solution.

It is difficult at the present time to know what is the contribution of each possibility. Work is in progress along this line.

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