863. *The Principles Governing High-temperature Ethane Cracking.*

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The kinetics of cracking of ethane in the presence of labelled $^{14}CH_4$ (~2%) at 90 mm. and 770—880° was studied in detail, the contents of the reaction vessel being rapidly mixed. Rate constants for the overall process were obtained, as well as for basic elementary reactions occurring in cracking. The chain part of ethylene formation by the conventional scheme did not exceed 10%.

THE evolution of the modern kinetic cracking theory was based on the radical-chain theory first applied to cracking by Rice. Apart from the elaboration of many logical schemes, this evolution proceeded in two largely independent directions. One was concerned with experiments carried out in order to investigate the principles governing free-radical reactions at relatively low temperatures and to determine corresponding activation energies and pre-exponential factors. The second involved investigations on a number of overall cracking effects at temperatures of 500—600°, seeking to obtain quantitative confirmation (or refutation) of the suggestion that cracking proceeds solely by a chain mechanism.[1] Direct determination of the cracking rate constant in terms of a definite mechanism, by means of formulæ for elementary constants derived from measurements over a temperature range where cracking was virtually absent, was not commonly attempted. This was largely due to lack of sufficiently accurate data. At the same time it was difficult to draw reliable, unambiguous conclusions from studies of overall effects at high temperatures. Consequently, notwithstanding a considerable advance in the elucidation of a wide range of phenomena, made possible by application of the radical-chain theory, there is still no general agreement as to whether thermal paraffin decomposition over a temperature range up to 650° proceeds solely by a chain mechanism, or by molecular processes as well.[1]

Considerable success has now been attained in the theoretical treatment of free-radical reactions.[2] As shown by a variety of experimental results, the reaction rate constants of basic radical reactions (metathesis, recombination, disproportionation) over the cracking temperature range involve small steric factors of the order of 10^{-3}—10^{-5}, decreasing with rise of temperature. Evaluation of these factors has shown that extrapolation from low-temperature reaction rate constants to cracking temperatures, by the Arrhenius equation, appears to be unjustifiable.

In view of the above, simultaneous verification of main kinetic characteristics, and direct determination of constants for basic elementary reactions at cracking temperatures seemed to be a pressing problem. Of special interest was the study of cracking at temperatures of 800—1000° C, since this temperature range corresponds to conditions concerned in the industrial production of olefins.[3]

The present work is concerned with the determination of the most important kinetic characteristics in ethane cracking at 770—900° C. Evaluation of rate constants for basic elementary reactions and direct determination of the relationship between molecular and radical-chain reaction rates were made by means of an ingenious technique, making use of a turbulent reactor and of labelled atoms.

EXPERIMENTAL

Investigation of cracking at temperatures above 700° requires a technique considerably different from that worked out for more moderate temperatures. The basic problem encountered in high-temperature experiments is to provide a heat supply that would be rapid enough to ensure a warming-up period shorter than the time needed for completion of the reaction.*

In contrast to the majority of earlier investigations on cracking in which external heating through reactor walls was used, somewhat as in industrial tubular furnaces, high-speed heating was achieved by contact of the products with small particles of a warm fluidized bed of the heat carrier.

As already shown [3] the mixing of raw material and heat-carrier streams at sufficiently high relative rates will diminish the heating time to 10^{-3}—10^{-4} sec. Low values for heating times can also be obtained by use of a stationary and a fluidized bed. This permits investigation of reactions completed in 10^{-2} and even 10^{-3} sec.

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* It will be noted that many investigations were vitiated by failure to deal with difficulties arising at high temperatures.

[1] Hinshelwood, *Science*, 1959, **125**, 679; Poltorak and Voevodsky, *Doklady Akad. Nauk S.S.S.R.*, 1950, **91**, 589; Stepukhovich, " Problems of Chemical Kinetics, Catalysis, and Reactivity " (Collected works in Russian), Moscow, 1955, Academy of Sciences of the U.S.S.R., p. 159.

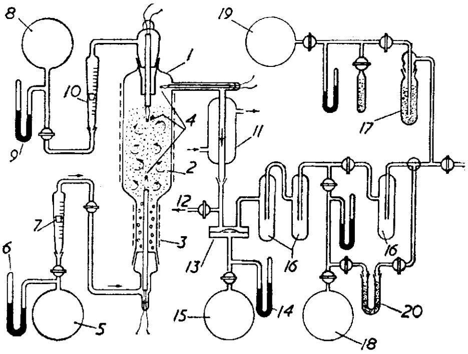
[2] Stepukhovich, *Uspekhi Khim.*, 1956, **25**, 263; Kondratiev, " Kinetics of Gas Reactions," Moscow, U.S.S.R. Academy of Sciences, 1958; Steacie, " Atomic and Free Radical Reactions," 1954, Reinhold Publ. Corp., New York; Trotman-Dickenson, *Quart. Rev.*, 1953, **7**, 198; Semenov, " Some Problems of Chemical Kinetics and Reactivity," Princeton Univ. Press, 1958.

[3] Lavrovsky and Brodsky, " A Physico-chemical Investigation of High-speed Contact Cracking," Reports to the Fourth World Petroleum Congress, Rome, Vol. V.

The vacuum apparatus with a fluidized bed reactor was designed for studying fast high-temperature endothermic reactions at constant concentrations and temperatures in the reaction zone. This appears considerably to simplify kinetic studies and the interpretation of results.

The apparatus is illustrated in Fig. 1. The feed gas was kept in bulbs (5) of 40 l. overall capacity. The amount of gas admitted into the reaction zone was adjusted by means of a tap. The gas supply rate was established from readings obtained with a rotameter (7) operating in vacuum and calibrated with respect to the working mixture, pressure measurements being made simultaneously. The fall of pressure in (5) during the experiment did not exceed 5 mm. Hg. The relative error in rate measurements did not usually exceed 3%.

FIG. 1. *Apparatus.*



The reaction vessel was operated as follows. Gas was preheated in the lower part of the quartz vessel (3) packed with quartz fragments. The temperature of the preheating element did not exceed 400°. Cracking took place in the middle of the vessel (2) in a fluidized bed of powdered corundum acting as heat carrier and convecting heat from the wall into the bulk. The effective diameter of corundum particles was varied in different experiments from 0·1 to 0·8 mm. depending upon the velocity of the gas stream. Rapid cooling of the products after liberation of gas from the fluidized bed was accomplished by admitting cold carbon dioxide from bulb (8) into the reaction vessel over the layer. The ratio of cracking gas to carbon dioxide was 1 : 5 (by weight).

Heating was by electrically heated wiring round the quartz tubes. Temperature measurements in the upper and lower part of the reaction zone * and over it were made by platinum-platinum-rhodium thermocouples [4] with uncovered junctions. Thermocouple readings were registered by a high-speed electron potentiometer. Temperature was set with an accuracy of ±2—3%. Pressure was maintained constant by means of a valve (13) introduced into the vacuum line beyond the reaction vessel and similar to that already described.[4] Simultaneous use of the valve and the rate-measuring rotameter ensured constant pressure and velocities of streams in the reactor at high rates for the short duration of the processes investigated.

Before experiments were started, the apparatus was evacuated by means of a diffusion vacuum pump to 5×10^{-4} mm. Hg, the reaction vessel was heated to the required temperature, and necessary counterpressure was established at the valve. The cracked gas from (5) was then admitted into the reaction vessel *via* the capillary taps, and carbon dioxide was supplied to the zone over the fluidized bed. This resulted in a 200—250° fall of temperature over the reaction zone as compared to the fluidized bed. As proved by special experiments, the cooling carbon dioxide did not penetrate into the reaction zone.

The first portions of gas from the reactor were voided to waste (12) until a stationary state was established in the reactor. The pressure in the reactor was kept 5—10 mm. Hg lower than the counterpressure at the valve, so that reaction products could not penetrate into the line of working traps through the valve. After establishment of a stationary state the line to waste

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* Agreement in temperature values for the upper and the lower part of the reaction zone was taken as a check on complete intermixing in the course of the reaction.

[4] Sharvin, *Zavod. Lab.*, 1955, **21**, 1261.

was cut off, the reactor pressure attained its operating value, and the valve opened automatically. A stopwatch was switched on simultaneously. The time of a run was usually 10—30 sec. As soon as the run was completed, the line of main traps was cut off, the watch stopped, and the reaction vessel again connected to waste.

Products that had passed *via* the valve were directed towards corresponding traps. The first three traps (16) were cooled with liquid nitrogen. Methane and hydrogen were collected in a fourth trap (17) filled with activated charcoal and also cooled by liquid nitrogen. After a run was completed, the first three traps were cut off from the fourth one, and the gas condensed therein was evaporated into a bulb (18). To ensure complete desorption of methane and hydrogen from the charcoal the fourth trap was heated after the experiment in a furnace at 200—250°. Desorbed methane and hydrogen were collected in a bulb (19). The overall volume of gases, and also the ratio of products condensable and non-condensable in liquid nitrogen, were determined by pressure in vessels of known volumes. Carbon dioxide was removed from the fraction condensable in nitrogen by pumping through a trap (20) packed with ascarite; this amount of condensable products was then again measured, and all gases were submitted to chromatographic analysis and separation. The analytical technique by means of gas-liquid chromatography has been described.[5]

After completion of the experiment a coke deposit formed on the heat carrier in the reaction vessel was removed by heating to 800°, the oxygen pressure being 500 mm. Hg. The gases thus formed were passed through traps cooled in liquid nitrogen, and carbon dioxide was condensed therein. After removal of the coke deposit, hydrogen was admitted into the reactor and remained there for 1·5—2 hr. at 900°.

Experiments on ethane cracking were conducted with small additions of labelled methane $^{14}CH_4$. Radioactivities of the resulting gases were measured by a 250 n.cm.^{3} internal Geiger counter. The pressure of hydrocarbon within the counter was kept at 80 mm. Hg. The ethane-labelled methane mixture was prepared in bulk for a series of experiments, in special vessels.*

The ethane was obtained by electrolysis of sodium acetate, and purified by passage through bromine-water, alkali, and a drying mixture, with subsequent manofold freezing in a trap immersed in liquid nitrogen, the non-condensable gases being removed by a diffusion pump. The ethane so obtained was pure to within the accuracy of chromatographic analysis.

A series of kinetic studies of ethane cracking was carried out at temperatures from 770° to 900°, a pressure of 90 ± 2 mm. Hg, and reaction times from 0·008 to 0·8 sec. As shown by special experiments, small additions of methane exert no influence on the ethane cracking process. The reduced reaction time † was calculated by the formula $t = VT_0p\varepsilon/T\alpha p_0w$, where V (cm.^{3}) is the value for the heat carrier charge of the reactor, w (cm.^{3}/sec.) is the volume rate of the gas supply, $T_0 = 290°$ K, T is the temperature throughout the experiment (in °K), p is the reactor pressure in mm. Hg, $p_0 = 760$ mm. Hg; α is a factor to allow for gas expansion brought about by increase in volume during the experiment, and ε is a fraction of the free volume, taken as 0·5.

Gas compositions obtained at 770°, 840°, and 890° are summarized in Table 1.

In addition to the products shown in Table 1, traces of propane and propene (~0·05%), butane, butenes, bivinyl ($\sum C_4 \simeq$ 0·05—0·1%), and acetylene (~0·01%) were found in the cracked gases by tracer analysis. The kinetics of the formation of these gases could be followed only by observing the accumulation of radioactivity in corresponding fractions, since the amounts of gas were too small to permit direct precise analytical determinations.‡ As shown by the radioactivity ratio, 50—60% of the C_3 fraction, present in vanishingly small amounts, is represented by C_3H_8, and 50—40% by C_3H_6. The main part of the C_4 fraction at 890° consisted

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* The majority of runs with labelled methane additions were conducted with mixtures of 98% C_2H_6 and 2% $^{14}CH_4$ (the activity of the mixture being $5{\cdot}35 \times 10^3$ counts/n. cm.^{3} min.) and of 97% C_2H_6 + 3·0% $^{14}CH_4$ (activity $2{\cdot}83 \times 10^4$ counts/n. cm.^{3} min.).

† The given value having a dimension of time should not be identified with the reaction time in the sense adopted for a reaction proceeding in a closed vessel.

‡ Radioactivities of C_3, C_4, and acetylene were measured as follows. Corresponding inactive gases were added to the mixture studied, and the mixture was then separated in a chromatographic column. The radioactivities of separated fractions of C_3, C_4 and C_2H_2 were then measured, and concentrations of radioactive gases in each mixture were determined from radioactivity values.

[5] Brodsky, Kalinenko, and Lavrovsky, *Khimia i technologya topliva*, 1956, No. 8, 18.

TABLE 1. *Composition of cracking products.*

Reduced reaction time (sec.)	Expansion coefficient (α)	Composition of cracking products (molar %) C_2H_6	C_2H_4	CH_4	H_2	Coke (CO_2)
Initial mixture: 98·0% of C_2H_6 + 2·0% of CH_4. At 770° ± 2°						
0·06	1·06	86·6	5·4	2·6	5·05	0·35
0·08	1·055	88·7	4·4	2·5	4·3	0·1
0·14	1·075	84·5	6·9	2·8	5·4	0·4
0·185	1·13	79·7	8·6	2·5	8·6	0·3
0·26	1·12	76·1	10·3	2·5	10·3	0·4
0·415	1·17	68·7	14·2	3·4	13·3	0·4
0·72	1·23	60·0	19·5	2·8	16·7	1·0
0·82	1·36	51·0	22·4	4·1	21·7	0·8
At 840° ± 2·0°						
0·008	1·04	89·0	4·5	2·0	4·3	0·2
0·0415	1·25	59·5	18·3	4·0	17·9	0·3
0·0625	1·27	55·7	21·1	3·9	19·0	0·3
0·0735	1·38	45·3	25·6	4·4	24·2	0·4
Initial mixture: 97% of C_2H_6 + 3% of CH_4. At 890° ± 2°						
0·0078	1·19	63·54	18·7	2·2	15·5	0·06
0·0117	1·23	58·8	20·5	3·2	17·4	0·1
0·0152	1·34	48·6	24·1	3·4	23·7	0·2
0·0156	1·38	50·2	22·5	4·2	22·6	0·5
0·0192	1·35	47·5	25·1	3·7	23·55	0·15

TABLE 2.* *Ratio of the i-th component radioactivity contained in* 1 *cm.*^{3} *of the gas formed* (A_i) *to that in* 1 *cm.*^{3} *of the initial gas* (A_0).

t (sec.)	T (°C)	$A_i/A_0 \times 10^5$ $i = C_2H_6$	$i = C_2H_4$	$i = C_2H_2$	$i = C_3$	$i = C_4$	$i =$ Coke (CO_2)
0·14	770 ± 2	7·1 ± 3·3	5·4 ± 1·5	—	15·8	0·14	2·8 ± 0·1
0·185		8·6 ± 3·7	7·9 ± 1·9	—	38	0·65	—
0·26		14·4 ± 5·6	13·8 ± 2·8	—	42·5	1·64	3·9 ± 0·2
0·415		19 ± 4·7	22 ± 1·9	—	74	3·5	6·35 ± 0·4
0·82		24 ± 5·6	52 ± 3·7		131	10·3	17·2 ± 0·9
0·008	840 ± 2	10·8 ± 5	9·3 ± 0·5	—	—	—	5·05 ± 0·1
0·026		80·5 ± 5	67·2 ± 2	—	—	—	14·4 ± 0·6
0·0415		80·5 ± 3	93·5 ± 5	—	140	—	28·8 ± 0·3
0·0625		86 ± 4	107 ± 3	—	—	—	30·7 ± 1·5
0·0735		76 ± 4	135 ± 5	—	250	—	—
0·0078	890 ± 2	87	146·5	—	248	9·75	0·35
0·0117		99	162	0·81	271	13·9	4·25
0·0152		126	247	2·04	400	24·2	17·3
0·0156		124	254	2·3	402	24·0	14·2
0·0192		138	297	4·08	477	39·5	13·2

* Where the error in radioactivity measurements is not shown it does not exceed 3% relatively. The radioactivity of the initial mixture was 5·35 × 10^3 counts/n.cm.^{3} min. at 770° and 840° c; 2·83 × 10^4 counts/n.cm.^{3} min. at 890° c.

TABLE 3. *Distribution of radioactivity in* C_3 *and* C_4 *fractions.*

(A_i/A_0) × 10^5

			C_3H_8		C_3H_6			C_4H_{10}		C_4H_8		C_4H_6	
T (°c)	t (sec.)	$A_{\Sigma C_3}$	$A_{C_3H_8}$	% of $A_{\Sigma C_3}$	$A_{C_3H_6}$	% of $A_{\Sigma C_3}$	$A_{\Sigma C_4}$	$A_{C_4H_{10}}$	% of $A_{\Sigma C_4}$	$A_{C_4H_8}$	% of $A_{\Sigma C_4}$	$A_{C_4H_6}$	% of $A_{\Sigma C_4}$
890	0·0156	402	200	51	190	49	24	2·2	9	12	50	9·8	41
830	0·057	136	69·5	58	50·5	42	12·8	—	—	—	—	—	—
800	0·115	85	54	67	27	33	5·25	—	—	—	—	—	—
782	0·185	40	—	—	—	—	3	1·2	40·1	1·0	33	0·8	27

of bivinyl (30—40%) and butenes (30—50%); at 782° its content in butane, butenes, and bivinyl was about the same.

Let us consider further the distribution of radioactivity in reaction products. Corresponding data for different temperatures at various reduced reaction times are given in Tables 2 and 3.

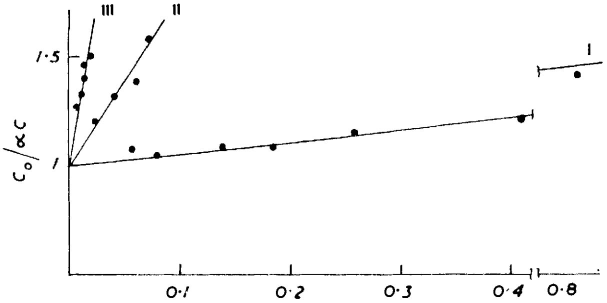
DISCUSSION

The values of the rate constants of the overall process were determined as follows. Consideration of the results obtained has shown [6] that intensive intermixing took place in the reaction vessel under the experimental conditions, and gas composition over the reaction zone was constant. Consequently, the overall cracking constant values k were determined from balanced equations, on the assumption that the cracking reaction is of first order with respect to $[C_2H_6]$:

$$[C_2H_6]_0 w_0 \cdot \frac{T}{T_0} \cdot \frac{p_0}{p} = [C_2H_6] \frac{T}{T_0} \cdot \frac{p_0}{p} \cdot w + k[C_2H_6]V\varepsilon$$

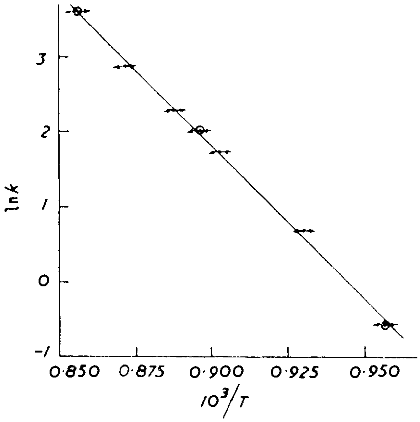
where $[C_2H_6]_0$ is the concentration of ethane in the initial mixture, $[C_2H_6]$ is the corresponding concentration in the reaction zone, w_0 (cm.^{3}/sec.) is the volume rate of the gas supply at the inlet to the fluidized bed, and w is the corresponding velocity at the reactor outlet, k is the cracking rate constant, and ε is the porosity.

FIG. 2. $C_0/\alpha C = [C_2H_6]_0/\alpha[C_2H_6]$ *as a function of* t.



(I) 770°, (II) 840°, (III) 890°.

FIG. 3. *ln* k *as a function of* 1/T



At $w_0 = w/\alpha$ and $t = V\varepsilon T_0 p/wTp_0$ (where α is a factor to allow for gas expansion caused by cracking and t is the reduced reaction time) we obtain from the balanced equation

$$[C_2H_6]_0/\alpha[C_2H_6] = 1 + kt$$

The overall cracking rate constant calculated from plots of Fig. 2 appeared to be 0·5 sec.$^{-1}$ at 770°, 6 sec.$^{-1}$ at 840°, and 30 sec.$^{-1}$ at 890°. Deviations from first order were not observed up to very high degrees of conversion. Consequently, self-inhibition of ethane cracking observed at lower temperatures, and increasing with the degree of conversion, was substantially diminished, if not absent, at least under the experimental conditions.

Fig. 3 is a plot of ln k versus $1/T$. The activation energy of the overall ethane cracking process calculated by this dependence was determined as $E = -\mathrm{d}\ln k/\mathrm{d}(1/T)$, and appeared to be 82 ± 1·5 kcal. over the temperature range investigated, the pre-exponential factor being 10^{16} sec.$^{-1}$.

Such an increase in activation energy as compared to the value of 69 ± 2 kcal./mole established at lower temperatures is of considerable interest. It may be naturally connected with a change in the overall mechanism of the process as the temperature is raised, and with the nature of temperature dependence of the unimolecular decomposition rate. This would also help to explain the empirical pre-exponential factor increase to 10^{16}.

It will be noted in this connection that the activation energy of the inhibited cracking

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[6] Brodsky, Kalinenko, and Lavrovsky, *Zhur. phys. Chim.*, 1960, **34**, 192.

reaction[7] is about 77 kcal./mole even at moderately high temperatures and approaches the value obtained by the authors for high-temperature conditions.

The absence of self-inhibition of ethane cracking under the experimental conditions, up to high degrees of conversion, is emphasized.

We now consider in detail the composition of the cracking products. As indicated in Table 1, a temperature rise would result not in an increase but in a slight decrease in CH_4 and coke yields at identical degrees of conversion. This is in agreement with previous results[3] on high-temperature cracking of gaseous alkanes and oil products obtained before, and with the conclusion that, with rise of temperature within certain limits and at a corresponding shortening of the contact time, the yield of main products (*e.g.*, olefins in the cracking of gaseous alkanes) will increase, and the yield of side products, particularly coke, will decrease.

In considering the above results on the distribution of radioactivity, the most important fact seems to be that maximum radioactivity is observed for the C_3 fraction. The specific radioactivity of this fraction is obviously particularly high. Its value could not be determined explicitly, since measurements of the amounts of C_3 formed in the course of the reaction were approximate and accurate only to within the ratio of 1·5—2. Estimation of the C_3 specific radioactivity gives values exceeding those of C_2H_6 and C_2H_4 by 2 or 3 powers of ten. The specific radioactivity of the C_4 fraction is also very high and exceeds that of C_2 hydrocarbons by more than an order. The specific activity of C_2H_4 was slightly higher than that of C_2H_6 in all experiments. Apparently, labelled C_2H_4 was formed not only from C_2H_6 but also from more active C_3 and C_4 as well. The specific radioactivity of coke is also substantially higher than that of C_2H_4 and C_2H_6. Hydrocarbons of a higher molecular weight also seem to participate in its formation.

As shown by analysis of $C_3{}^*$ and $C_4{}^*$ fraction compositions (Table 3), 50—60% of the $C_3{}^*$ fraction was represented by $C_3{}^*H_8$ and 50—40% by $C_3{}^*H_6$, whilst the main activity of $C_4{}^*$ was found in bivinyl (30—40%) and butene (30—50%).*

Consideration of experimental results on the distribution of activity in reaction products leads to a direct qualitative conclusion on the occurrence of radical reactions in the system investigated. This is in keeping with earlier studies. Indeed, radioactivity was found in reaction products that could hardly be conceived to be formed from labelled methane in a way other than by the radical mechanism. However, quantitative treatment would be necessary to estimate the rôle of radical reactions in the overall cracking process.

On the basis of the conventional radical-chain scheme the following reactions may be considered to occur at high temperatures in the given system involving ethane and additions of labelled methane.

Chains were initiated essentially by the splitting of C_2H_6 into two methyl radicals: †

$$\text{(i)}\quad C_2H_6 \longrightarrow 2CH_3;\ k_1$$

This was followed by reactions of the type ‡

$$\text{(ii)}\quad C_2H_6 + CH_3 \longrightarrow CH_4 + C_2H_5;\ k_{2(CH_3,C_2H_6)}$$

Recombination of hydrocarbon radicals proceeded homogeneously and by binary collisions; in hydrogen-atom recombination the main part was played by three-body collisions:

$$\text{(iii)}\quad \left\{ \begin{array}{ll} R_1 + R_2 \longrightarrow R_1R_2; & k_3 \\ R + H \longrightarrow RH; & k_3{}' \\ 2H + M \longrightarrow H_2 + M; & k_3{}'' \end{array} \right.$$

(R may be CH_3, C_2H_5, or C_3H_7)

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* Molecules containing a radioactive ^{14}C atom are denoted here and hereinafter by an asterisk.

† The chain initiation reaction $C_2H_6 \longrightarrow C_2H_5 + H$ will be neglected here.

‡ Constants are defined in accordance with the reaction order of the radical-chain scheme.

[7] Steacie and Shane, *Canad. J. Res.*, 1940, *B*, **18**, 351.

The chain-propagation reaction proceeded by ethyl-radical decomposition:

$$\text{(iv)}\ C_2H_5 \longrightarrow C_2H_4 + H;\ k_4$$

Finally, a disproportionation reaction took place:

$$\text{(v)}\ 2C_2H_5 \longrightarrow C_2H_6 + C_2H_4;\ k_5$$

The formation of active methyl radicals from initially labelled methane could occur by reactions

$$\begin{aligned} &C^*H_4 + R \longrightarrow C^*H_3 + RH; && k_2 \\ &C^*H_4 \longrightarrow C^*H_3 + H; && k_{1a} \end{aligned}$$

Since cracking was investigated under conditions of intensive mixing, concentrations of intermediate and end-products may be determined simply by writing conservation equations accounting for the withdrawal, formation, and disappearance reactions of corresponding products.

Averaged values for constants of similar reactions were used in some cases, for the sake of simplicity. For instance, investigations on reactions such as $R_i + R_2H \longrightarrow R_iH + R_2$ were made by using the constant

$$\bar{k}_2 = \sum_i k_{2(R_i,RH)} \frac{[R_i]}{\sum [R_i]}$$

A mean value of $\bar{k}_3$ was used for the overall radical-recombination reaction, including hydrogen atoms.

In accordance with the given scheme, and ignoring the balanced equation for free-radical concentration, we obtain

$$[R]/t - (2k_1[C_2H_6] - 2\bar{k}_3[R]^2) = 0$$

Whence

$$[R] = [\surd(1 + 16\, k_1\bar{k}_3[C_2H_6]t^2) - 1]/4\bar{k}_3 t \qquad (1)$$

Expressions

$$[CH_3] = \frac{(2k_1[C_2H_6] + \bar{k}_2[R_i][CH_4])t}{1 + k_{2(CH_3,M)}[M]t + \bar{k}_3[R]t} \qquad (2)$$

and

$$[C_2H_5] = \frac{\bar{k}_2[C_2H_6][R_i]t}{1 + k_{2(C_2H_5,M)}[M]t + \bar{k}_3[R_i]t + k_4t} \qquad (3)$$

are derived in a similar way.* Here [M] and [R] are concentrations of molecules and radicals respectively in the system.

Hence a formula describing variations in labelled methyl-radical concentrations with change of t will be written as

$$[C^*H_3] = \frac{(\bar{k}_2[C^*H_4][R_i] + k_{1a}[C^*H_4])t}{1 + k_{2(CH_3,M)}[M]t + \bar{k}_3[R_i]t} \qquad (4)$$

In studying the mechanism of formation of labelled products, allowance should be made for the fact that in the case considered the radioactivity of methane in the reaction mixture was about 10^5—10^6 times that of all other products, and consequently the concentration of C^*H_3 was considerably in excess over that of all other active radicals.

Thus the formation of labelled ethane could proceed by reactions

$$\begin{aligned} &CH_3 + C^*H_3 \longrightarrow C_2^*H_6 \\ &C_2^*H_5 + C_2H_6 \longrightarrow C_2^*H_6 + C_2H_5 \\ &C_2^*H_5 + C_2H_5 \longrightarrow C_2^*H_6 + C_2H_4 \end{aligned}$$

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* The introduction of identical $\bar{k}_2$ values into (2) and (3) corresponds to the definition of the given constant with an accuracy to within 2 (Vedeneev, *Doklady Akad. Nauk S.S.S.R.*, 1957, **114**, No. 3, 571).

However, if allowance is made for the high concentration of $[C{*}H_3]$, comparative estimation of the amounts of $C_2{*}H_6$ formed by this reaction would show that labelled ethane is formed essentially by the first route. Consequently only this route was taken into account in calculations. The following equation was obtained: *

$$[C_2{*}H_6] = k_3[CH_3][C{*}H_3]t/(1 + kt) \qquad . \; . \; . \; . \; . \quad (5)$$

Similarly, labelled products forming the $C_3{*}$ fraction were obtained on recombination of $C{*}H_3$ and C_2H_5.

The reaction involving formation of $C_3{*}$ by the scheme

$$\text{(vi)} \quad C{*}H_3 + C_2H_4 \longrightarrow C_3{*}H_7 \longrightarrow C_3{*}; \; k_{11}$$

can be neglected here, since at the high temperatures investigated the equilibrium of the given reaction is shifted completely to the left, and since the corresponding rate constant value is relatively small. It will also be noted that the $C_3{*}$ fraction composition is in support of the suggestion that its formation occurs essentially by a recombination of $C{*}H_3$ and C_2H_5. Indeed, a reaction of this type would yield propane, and reaction (vi) essentially propene, whilst under the investigated conditions 50—60% of the $C_3{*}$ fraction was represented by $C_3{*}H_8$ and 40—50% by $C_3{*}H_6$, the latter being essentially, if not entirely, a product of $C_3{*}H_8$ cracking.

In accordance with the adopted mechanism of the $C_3{*}$ fraction formation, the accumulation of this fraction in the course of the reaction is described by the equation:

$$[C_3{*}] = k_3[C{*}H_3][C_2H_5]t/[1 + f_{C_3}(t)t] \qquad . \; . \; . \; . \; . \quad (6)$$

where $f_{C_3}(t)$ is the rate function of the disappearance of the C_3 fraction at a concentration equal to unity.

The formation of active hydrocarbons in the $C_4{*}$ fraction could occur by several routes:

$$\begin{aligned}
&\text{(iiia)} \quad C_2{*}H_5 + C_2H_5 \longrightarrow C_4{*}H_{10} \\
&\text{(iiib)} \quad C{*}H_3 + C_3H_7 \longrightarrow C_4{*}H_{10} \\
&\text{(via)} \quad C_2{*}H_5 + C_2H_4 \rightleftharpoons C_4{*}H_9 \longrightarrow C_4{*} \\
&\text{(vib)} \quad C_2H_5 + C_2{*}H_4 \rightleftharpoons C_4{*}H_9 \longrightarrow C_4{*} \\
&\text{(viia)} \quad C_2{*}H_4 + C_2H_6 \longrightarrow C_4{*}H_8 + H_2 \\
&\text{(viib)} \quad C_2H_4 + C_2{*}H_6 \longrightarrow C_4{*}H_8 + H_2 \\
&\text{(viic)} \quad C_2H_4 + C_2{*}H_4 \longrightarrow C_4{*}H_8
\end{aligned}$$

If $C_4{*}$ were formed by reactions (vii), the $C_4{*}$ fraction specific radioactivity would not exceed that of $C_2{*}H_6$ and $C_2{*}H_4$. But in reality the specific radioactivity of $C_4{*}$ is 10—15 times that of $C_2{*}H_6$ and $C_2{*}H_4$. Consequently, the molecular mechanisms of the $C_4{*}$ fraction formation will be of secondary importance in the case considered. The formation of active hydrocarbons of the $C_4{*}$ fraction by reactions (via and b) can be ruled out for the same reasons that were suggested for the discarding of reaction (vi) in the formation of $C_3{*}$. Let us further consider independently the possibility of $C_4{*}$ formation by reactions (iiia and b), the $C_4{*}$ concentration being represented by equations

$$[C_4{*}] = k_3[C_2{*}H_5][C_2H_5]t/[1 + f_{C_4}(t)t] \qquad . \; . \; . \; . \; . \quad (7)$$

$$[C_4{*}] = k_3[C{*}H_3][C_3H_7]t/[1 + f_{C_4}(t)t] \qquad . \; . \; . \; . \; . \quad (7a)$$

where $f_{C_4}(t)$ is a function of the $C_4{*}$ disappearance rate.

If (iiib) is assumed, according to (6) and (7*a*) the ratio of C_3 to C_4 concentrations should be

$$\frac{[C_2H_5]}{[C_3H_7]} \leqslant \frac{[C_3{*}]}{[C_4{*}]} = 10\text{—}20$$

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* According to ref. 8, the isotope effect brought about by change of the cracking constant k on transition from C_2H_6 to $C_2{*}H_6$ amounts to some 10%. Since such deviations are within the accuracy of determination, no distinction will be made hereinafter in labelled and unlabelled compounds.

[8] Brodsky, Kalinenko, and Lavrovsky, *J. Appl. Rad. and Isotopes*, in the press.

at $1 + f_{C_4}(t)t \geqslant 1 + f_{C_3}(t)t$, as under experimental conditions the concentration of C_3H_8 did not exceed 0·05—0·1% and since C_3H_7 radicals are formed from C_3H_8. But in reality $[C_3^*]/[C_4^*] > 10^2$. Thus the reaction (iiia) of ethyl-radical recombination should be considered as the main route of C_4^* formation.

As stated before, the specific activity of $C_2^*H_4$ exceeded that of $C_2^*H_6$ in all experiments, so that ethane could not be the main source of formation of active ethylene. Considerable amounts of $C_2^*H_4$ were apparently yielded by propane in particular in accordance with scheme

$$\begin{tikzcd} C^*H_3 + C_2H_5 \arrow[r] & C_3^*H_8 \arrow[r] & CH_3 + C_2^*H_5 \arrow[d] \\ & & C_2^*H_4 + H \end{tikzcd}$$

Consequently the overall amount of the active ethylene yield was determined from the equation

$$[C_2^*H_4] = kt[C_2^*H_6] + \tfrac{1}{2}(k_3[C^*H_3][C_2H_5]t - C_3^*) \quad . \quad . \quad . \quad . \quad (8)$$

the $\frac{1}{2}$ factor being characteristic of the statistical probability of $C_2^*H_4$ formation from $C_3^*H_8$.

In calculating elementary reaction rate constants, balanced equations of stable products involving radical concentrations as a function of t, were correlated with experimental curves. The chosen combinations of experimental values were linearly dependent on t. For the sake of brevity, detailed analysis will not be discussed here. Rate constants for elementary reactions and their combinations summarized in Table 5 were obtained in this way.

Concentrations of CH_3, C_2H_5, and C^*H_3 radicals given in Table 4 were obtained from (2), (3), and (4).

As seen from Table 4, it may be assumed that $[R] = \sum[R_i] \cong [CH_3] + [C_2H_5]$, *i.e.*, CH_3 and C_2H_5 radicals represent the main radicals in the reaction system.

TABLE 4. *Radical concentrations (per cm.³) in ethane cracking.*

Radicals	770°	840°	890°
$[R] = \Sigma[R_i]$	$2·6 \times 10^{13}$	10^{14}	3×10^{14}
$[CH_3]$	5×10^{12}	5×10^{13}	$7·8 \times 10^{13}$
$[C_2H_5]$	$2·5 \times 10^{13}$	$1·9 \times 10^{14}$	$3·4 \times 10^{14}$
$[C^*H_3]$	$3·7 \times 10^{10}$	$2·8 \times 10^{11}$	$3·8 \times 10^{11}$

TABLE 5.* *Reaction rate constants in ethane cracking as determined from experimental results.*

		$PZ \exp(-E/\boldsymbol{R}T)$				
Constants	Reactions	PZ	E	770°	840°	890°
k	$C_2H_6 \longrightarrow C_2H_4 + H_2$	$6·9 \times 10^{16}$	82	0·5	6·0	30·0
k_1	$C_2H_6 \longrightarrow 2CH_3$	10^{14}	82	$6·6 \times 10^{-4}$	$7·8 \times 10^{-3}$	$4·4 \times 10^{-2}$
$k_{2(CH_3.M)}$	$CH_3 + C_2H_6 \longrightarrow$ $\longrightarrow CH_4 + C_2H_5$	7×10^{-14}	12	$2·2 \times 10^{-16}$	$2·8 \times 10^{-16}$	4×10^{-16}
$\bar{k}_2/\bar{k}_3$				$2·5 \times 10^{-3}$	$1·2 \times 10^{-2}$	$3·3 \times 10^{-2}$
k_3	$R_1 + R_2 = R_1R_2$			5×10^{-13}		
$\bar{k}_2$	$R_1(H) + R_2H \longrightarrow$ $\longrightarrow R_1H(H_2) + R_2$			$1·2 \times 10^{-15}$	$3·5 \times 10^{-15}$	$5·3 \times 10^{-15}$
$k_3/\bar{k}_3$				1	1·6	2·5
k_4	$C_2H_5 \longrightarrow C_2H_4 + H$	10^{10}	36·5	$2·2 \times 10^2$	6×10^2	$1·3 \times 10^3$
$100k_c/k$				2·4	3	3·3

* The concentration is taken in molecules/cm.³.

Now let us consider the part of chain reactions in ethane cracking under experimental conditions. In accordance with the conventional scheme, the reaction $C_2H_5 \longrightarrow C_2H_4 + H$ is commonly considered to represent the chain formation of C_2H_4 from C_2H_6.

The rate constant for the overall process of ethylene chain formation will consequently be written as

$$k_c = \frac{k_4[C_2H_5]}{[C_2H_6]} = \frac{k_4\bar{k}_2[R]t}{1 + k_{2(CH_3,M)}[M]t + \bar{k}_3[R]t + k_4t} \quad . \; . \; . \quad (9)$$

the chain reaction part being represented by k_c/k, where k is the experimental overall constant of ethane cracking.

Calculation of k_c/k by the above formula shows that formation of C_2H_4 by a chain reaction amounts only to 2—3 per cent over the entire temperature range. Since this calculation does not account for the difference in averaged rate constant values for metathetic reactions of radicals with CH_4 and C_2H_6 molecules, the above value might prove to be slightly higher, but not more than by a factor of 2—3.

The upper limits of k_c values were determined independently, by using only experimental values. Thus the following relationship was obtained by means of (6) and (7):

$$\frac{[C_4^*]}{[C_3^*]} = \frac{1 + f_{C_3}(t)t}{1 + f_{C_4}(t)t} \cdot \frac{[C_2^*H_5]}{[C^*H_3]} \quad . \; . \; . \; . \; . \; . \; . \quad (10)$$

Accounting for

$$1 + f_{C_4}(t)t > 1 + f_{C_3}(t)t \quad . \; . \; . \; . \; . \quad . \quad (11)$$

and

$$[C_2^*H_4] > k_4[C_2^*H_5]t$$

we obtain

$$k_c = \frac{k_4\bar{k}_2[R]t}{1 + k_{2(CH_3,M)}[M]t + \bar{k}_3[R]t + k_4t} < \frac{[C^*H_3]k_4}{[C^*H_4]} < \frac{[C_3^*][C_2^*H_4]}{[C_4^*][C^*H_4]t} \quad . \quad (12)$$

It follows from this inequality, upon introduction of experimental values, that at 770° the formation of C_2H_4 by chain reaction did not exceed 7%, and at 890° 2% of the overall C_2H_4 formation rate.

Thus, as confirmed by two independent calculations, the formation of C_2H_4 from C_2H_6 by a conventional chain mechanism does not exceed 5—10% under our experimental conditions and over the range of temperatures investigated.

It must be emphasized that in accordance with data obtained for the above temperature range, generalized steric factors for basic radical reactions of cracking appear to be very low (10^{-3}—10^{-4}). Thus a value of 5×10^{-13} was obtained for the recombination constant in accordance with above calculations. Allowance being made for the negative coefficient of the given reaction constant,[9] it may be seen that the commonly accepted steric recombination factor of unity will be valid only at temperatures near that of the room. The metathetic reaction constant for $CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$ is also in agreement with the low steric factor value of 7×10^{-4}, in accordance with work quoted in ref. 2.

A similar steric factor will be obtained for an average rate constant k_2 of a metathetic reaction. Allowance should only be made for the fact that the temperature coefficient of the constant

$$\bar{k}_2 = k_{2(H,M)}\frac{[H]}{[R]} + k_{2(CH_3,M)}\frac{[CH_3]}{[R]} + k_{2(C_2H_5,M)}\frac{[C_2H_5]}{[R]}$$

is essentially dependent on increase in hydrogen-atom concentration with temperature, since $k_{2(H,M)} > k_{2(CH_3,M)}, k_{2(C_2H_5,M)}$.

The pre-exponential factor value for k_4 obtained in this work appeared to be 10^3 times lower than the commonly accepted value of 10^{13}. It will be noted, however, that values of k_4 were determined by means of complicated indirect calculations and were less precise than calculations made for other constants.

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[9] Ingold and Lossing, *J. Chem. Phys.*, 1953, **21**, 368, 1135.

However, the general conclusion as to the small part played by the conventional radical-chain mechanism does not depend on k_4, which enters into both the nominator and the denominator of (12). It will also be noted that the measured radical concentrations are near to equilibrium, and this is additional evidence for the absence of inhibiting effect by the wall.

It is noteworthy that C_3 and C_4 hydrocarbon fractions obtained in ethane cracking in minor amounts were undoubtedly formed by the radical route under the conditions investigated. This follows from the high specific radioactivity values noted above, and is essential for the understanding of cracking-inhibition effects exerted, for instance, by additions of nitric oxide. The complicated nature of this phenomenon is confirmed by the fact that nitric oxide does not inhibit C_4 formation in cracking, as observed by Silcocks.[10] It was obviously erroneous to ascribe it to a molecular formation mechanism.

The overall relative increase in the radioactivity of high-molecular and condensed products (coke) is in support of the prevailing chain mechanism of secondary cracking reactions under experimental conditions.

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[10] Silcocks, *Proc. Roy. Soc.*, 1956, *A*, **233**, 465.