293. *The Kinetics of the Sulphonation of Nitrobenzene by Sulphur Trioxide.*

By D. R. VICARY and C. N. HINSHELWOOD.

For the correlation of electronic theories of organic reactions with theories of reaction velocity, further investigation of the mechanism of aromatic substitutions is needed. The sulphonation of nitrobenzene by sulphur trioxide has been found to be of the second order with respect to the latter, little influenced by sulphuric acid at higher temperatures, retarded by it at lower temperatures, uncomplicated by sulphone formation, and strongly retarded by the formation of a compound between the sulphur trioxide and the sulphonic acid. The activation energy is approximately 11,400 calories.

THE study of the kinetics of aromatic substitution reactions is of twofold interest. First, little work has hitherto been done which throws light on the specific mechanisms of these reactions. Secondly, the effect of substituents being most clearly interpreted in terms of the electronic theory of organic reactions, the kinetics of substitution reactions may help to a physical interpretation of this theory. It has already become clear from the study of other organic reactions that there is a connexion between the activation energy and the effects known as the inductive and electromeric effects.

The kinetic investigation of aromatic substitution is, however, difficult. Halogenation is usually either a photochemical or a heterogeneous catalytic reaction. The work of Benford and Ingold (J., 1938, 929) has shown that nitration may be a very complex process. Sulphonation should be less complicated, and the only side reactions are sulphone formation and a possible oxidising action of the sulphur trioxide. Under the conditions of the following experiments the latter was most improbable and the former was shown to be negligible.

The sulphonation reaction was studied by Martinsen (*Z. physikal. Chem.*, 1908, **62**, 713), who sulphonated *p*-nitrotoluene with oleum in large excess. He assumed a reaction of the type $H_2SO_4 + ArH = Ar{\cdot}SO_3H + H_2O$, and found that the bimolecular constants calculated on this basis fell as reaction proceeded : this he attributed to the accumulation of water in the system. Joffe (*J. Gen. Chem. Russia*, 1933, **3**, 437, 505) made certain corrections to these results and put forward a theory in which sulphuric acid, besides being a reactant, was also an acid catalyst and the cause of a back-reaction. The latter was assumed by analogy with the hydrolysis of α-naphthalenesulphonic acid by hydrochloric acid at 200°. Joffe's experimental work, however, did not confirm his theory. Lauer and his co-workers (*J. pr. Chem.*, 1932, **135**, 164; 1935, **142**, 258; **143**, 127; **144**, 32) have studied the sulphonation of anthraquinone and conclude that both sulphur trioxide and sulphuric acid contribute to sulphonation.

Choice of Conditions for the Quantitative Study of Sulphonation.—Preparative experience shows that sulphur trioxide is a much better sulphonating agent than sulphuric acid, and therefore it would appear that the best agent for use in kinetic investigations would be a solution of the trioxide in some solvent. Courtot and Bonnet (*Compt. rend.*, 1926, **182**, 855) employ chloroform as a solvent in sulphonation below 10°, but above that temperature it is attacked. Carbon tetrachloride is attacked in the cold, forming carbonyl chloride, and acetic anhydride reacts to form sulphoacetic acid. Hexane has been shown to be capable of direct sulphonation (Worstall, *Amer. Chem. J.*, 1898, **20**, 664). For the present purpose concentrated sulphuric acid itself was unsuitable as a solvent on account of the large excess of acid, which would make it impossible to follow the course of the reaction by titration. It was finally decided to use the substance to be sulphonated, namely, nitrobenzene, as its own solvent. Masson (J., 1931, 3200) has shown that sulphuric acid forms a complex with nitrobenzene and is readily soluble. Sulphur trioxide proved to be quite soluble in nitrobenzene, so that direct solution of the one reagent in excess of the other was chosen as the condition for studying the reaction.

EXPERIMENTAL.

Method.—Good commercial nitrobenzene was dried and fractionated several times. Sulphur trioxide was prepared for each experiment by distilling it in small portions from 60% oleum in a specially constructed all-glass apparatus into about 50 c.c. of solvent. The white fume dissolved in the nitrobenzene, giving a brown solution, which was pipetted into 2-c.c. or 5-c.c. tubes. These were sealed, and after known periods in a thermostat, their contents were analysed.

According to the equation $SO_3 + C_6H_5{\cdot}NO_2 = C_6H_4(NO_2){\cdot}SO_3H$ the acidity falls to one-half its initial value, a fact which allows the progress of the reaction to be followed by titration with alkali. In these experiments standard sodium hydroxide (about N/20) was used with methyl-red as indicator. Acetone was added to the titration mixtures to make them homogeneous. End-points were determined by keeping 5-c.c. portions at 121° for at least 24 hours. The products were analysed by extraction with water and benzene. The unchanged nitrobenzene went into the benzene layer and the acids into the aqueous layer. The benzene layer was washed with water, the washings added to the aqueous layer, and the whole titrated. This solution was boiled down to about 100 c.c. and analysed for sulphuric acid by gravimetric determination as barium sulphate.

The Question of Sulphone Formation.—In preparing a reaction mixture sulphuric acid may be distilled over in the fume, and sulphur trioxide will combine with any traces of water taken up by the nitrobenzene, so that a small amount of sulphuric acid is always present at the beginning of the reaction. This does not contribute to the sulphonation, as was shown by adding concentrated sulphuric acid to nitrobenzene and keeping them at 121°. The following figures, giving the titres of samples, show that the reaction of sulphuric acid is negligible compared with that of sulphur trioxide, which at this temperature has reacted completely within 24 hours.

Time, hours	0	4	7	24	46	168
Titre, c.c.	21·80	21·80	21·70	21·65	21·50	21·55

Thus we have the scheme :

$$\text{Initial } SO_3 = 2 \times \text{total fall in titre during reaction.}$$
$$\text{Initial } H_2SO_4 = \text{Initial titre} - (2 \times \text{total fall in titre}).$$

This assumes that no sulphone is formed, an assumption which needs justification, since the use of sulphur trioxide in the presence of an excess of the aromatic substance is a well-known method for the preparation of certain sulphones. The titration method by itself does not distinguish between sulphone formation and sulphonation.

$$\begin{aligned} &(a)\ RH + SO_3 = R{\cdot}SO_3H \\ &(b)\ 2RH + SO_3 = R{\cdot}SO_2R + H_2O \\ &\quad\ H_2O + SO_3 = H_2SO_4 \end{aligned}$$

Both (*a*) and (*b*) lead to the reduction of the titre to one-half. If the reaction $2R{\cdot}SO_3H = R_2SO_2 + H_2SO_4$ occurs, the titre remains unchanged. Gravimetric estimation of the sulphuric acid present at the end of the reaction will, however, show whether sulphone is formed to an appreciable extent, since reaction (*b*) yields sulphate, which could not be otherwise accounted for. In 36 experiments, analysis showed, as far as the accuracy of the method permitted, that the sulphuric acid present at the end of the reaction did not exceed that present initially. Table I contains some typical results. We therefore conclude that under the conditions of these experiments sulphone formation is negligible. This conclusion is supported by the work of Holleman (*Rec. Trav. chim.*, 1905, **24**, 194), who prepared the potassium salt of *m*-nitrobenzenesulphonic acid and recorded a trace only of sulphone, and by the work of Lauer, who prepared the pure sulphonic acid by the action of sulphur trioxide on nitrobenzene at 140°.

Experimental Errors.—In all experiments the end-point was determined at 121°, and 24 hours was shown to be long enough to reach it.

Time, hours	24	48	72	96
Titre, c.c.	40·90	41·00	40·90	40·90

The brown colour of the solution masked the colour change of the methyl-red to some extent, and for the end-point determinations bromothymol-blue was used. The initial titre might be misleading if any reaction due to local heating occurred as the sulphur trioxide dissolved in the nitrobenzene : this was investigated by measuring the initial titre of a mixture and analysing it gravimetrically. The following figures were obtained :

Initial titre, c.c. of N/20 = 220·0
Weight of $BaSO_4$, g. = 1·2449
Equivalent, in c.c. of N/20 = 213·3

Thus the error may be about 3%.

The reaction mixtures were fuming liquids, and in their manipulation there was always a certain loss. This was estimated by taking a sample, filling a reaction tube, and deliberately manipulating it so that there was a maximum loss of fume. The titre of the sample was compared with that of one taken and handled in the normal way. The difference was 2·80 c.c. in 76·7. The normal error was presumably much smaller than this. The errors in the barium sulphate precipitations were due to variation in the dilution and to the presence of organic material and colouring matter. Joffe's suggestion that acid would hydrolyse the sulphonic acid made it advisable to carry out the precipitation as quickly as possible, and also to vary the temperature conditions during precipitation. From a given sample when both solutions were boiling, 0·512 g. of barium sulphate was obtained, and when the barium chloride only was boiling, 0·519 g. Both solutions could not be used cold, since the precipitation of the sulphate was then unsatisfactory.

FIG. 1.

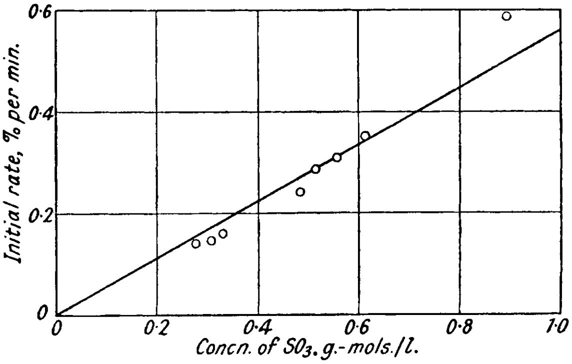
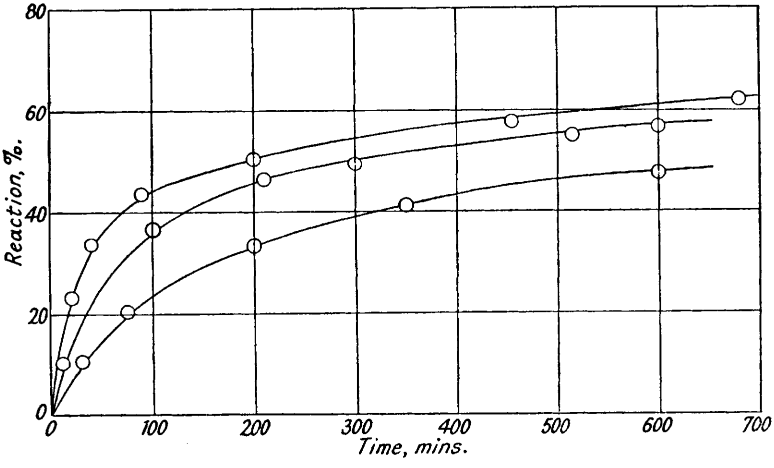


FIG. 2.



Runs with initial concentration of SO_3 = 1. 0·974 *g.-mol./litre.*
2. 0·679 ,, ,,
3. 0·286 ,, ,,

Kinetics.—(a) *Initial rates of reaction.* Table II shows the initial rates, those for 40° being plotted in Fig. 1, from which it can be seen that the reaction is approximately of the second order with respect to the sulphur trioxide. In Fig. 2 are some typical curves showing the marked retardation which sets in when the reaction has run about half its course. This retardation proves to be due to the formation of an addition compound between sulphur trioxide and the sulphonic acid. It is the more in evidence the lower the temperature.

(b) *The retardation.* In an ordinary bimolecular reaction we have $dx/dt = k(a - x)^2$, whence $\sqrt{(dx/dt)/(a - x)^2}$ is a constant; but if only a fraction, α, of the reactant is free to enter into the reaction, then $dx/dt = k\alpha^2(a - x)^2$, so that $\alpha = \text{const.}\ \sqrt{(dx/dt)/(a - x)^2}$. From reaction–time curves of the kind shown in Fig. 2, values of $\Delta x/\Delta t$ are taken and the values of $\sqrt{(dx/dt)/(a - x)^2}$ are plotted against the percentage change. The value of the expression for $x = 0$ is then scaled to unity and the other values in proportion. This gives a series of values of α for various values of x, since we may assume α to be unity when x is zero, that is, when there is no reaction product to combine with and remove sulphur trioxide. Curves showing the variation of α with x are given in Figs. 3 and 4.

FIG. 3.

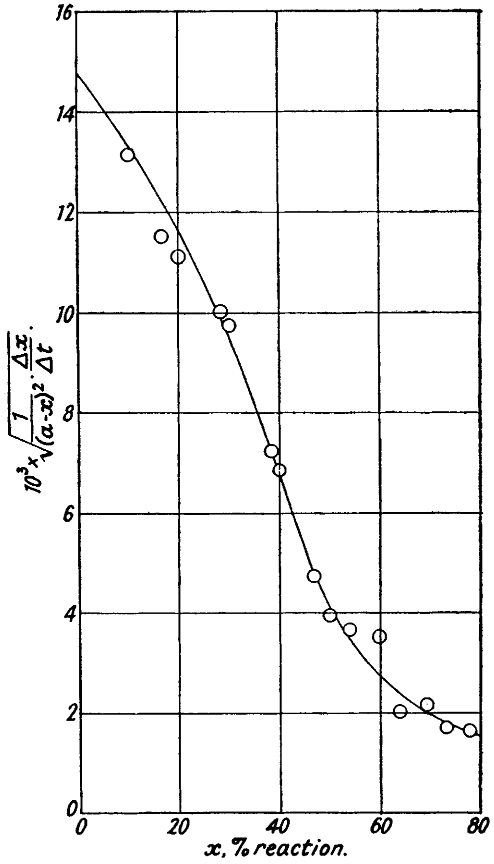
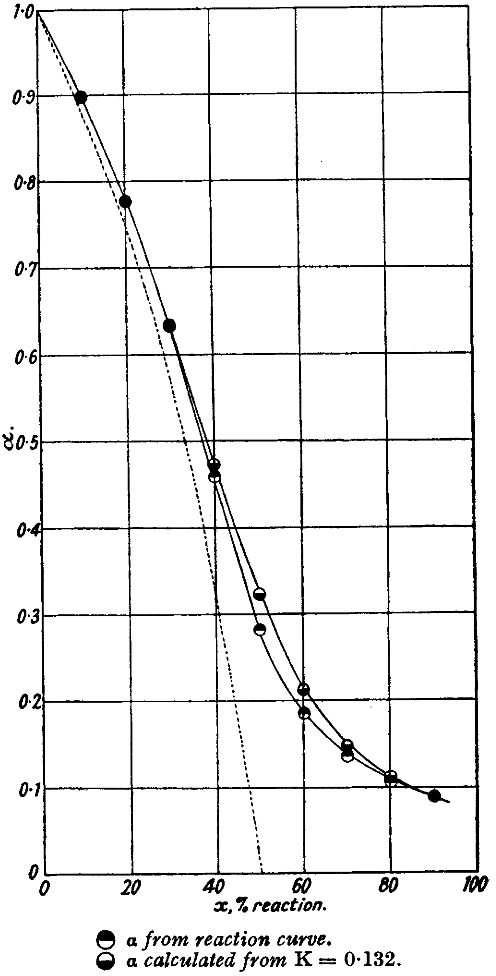


FIG. 4.



If a 1 : 1 complex is formed between sulphur trioxide and the sulphonic acid, we have the following equilibrium constant:

$$K = [\text{Complex}]/[\text{SO}_3][\text{Sulphonic acid}]$$

$[\text{Complex}] = (1 - \alpha)(a - x)$; $[\text{Free SO}_3] = \alpha(a - x)$

$[\text{Free sulphonic acid}] = [x - (1 - \alpha)(a - x)]$

$$K = (1 - \alpha)/\alpha[x - (1 - \alpha)(a - x)]$$

K can be calculated from the values of α, but since the equilibrium proves to lie very much on one side, the actual values are subject to great error. The same circumstance, however, provides that a value corresponding to $x = 50\%$ is accurate enough for the calculation of values of α over the whole course in fair agreement with experiment. This is shown in Fig. 4. Numerical data are collected in Table III. The dotted line in Fig. 4 shows the value which α would have if the compound formation were complete: from this it can be seen that the equilibrium favours compound formation. This means that the numerical values of K are not of much use for calculating the heat of formation of the compound.

Velocity constants for the whole course of an experiment can be calculated from the expression $k = (\Delta x/\Delta t)/(a - x)^2\alpha^2$ and agree with those obtained from the initial rates (Table IV).

(c) *Effect of added product.* Confirmation of the above explanation of the retardation was obtained by initial addition of reaction product. A portion of nitrobenzene was charged with sulphur trioxide in the usual way, allowed to react completely, and analysed. Some was then mixed with fresh nitrobenzene and used as solvent for a fresh charge of sulphur trioxide. If A is the initial sulphonic acid concentration, the equilibrium constant becomes $K = (1 - \alpha)/\alpha\{x - (1 - \alpha)(a - x) + A\}$, from which α and hence k can be calculated as before. The addition of the product reduced the reaction rate very markedly, but the values of k were comparable with those obtained in experiments without added product (Table V, and the values marked with an asterisk in Table IV).

(d) *Effect of added sulphuric acid.* At 80° no systematic retardation by added sulphuric acid could be detected. At 40° there was such a retardation, probably due to the conversion of some of the sulphur trioxide into pyrosulphuric acid which reacts less rapidly. The retardation caused by a large excess of added acid was, however, not great enough to allow the variations of the ordinary k values to be attributed to the varying small amounts of sulphuric acid initially present.

(e) *Temperature coefficient.* The values of k from the initial rates are subject to errors in drawing tangents to curves: those from the successive increments on the reaction–time curves, to errors arising from the smallness of the increments. Both sets are used in plotting the Arrhenius equation line. There is some drift in k with concentration; but the error is reduced by the fact that similar ranges are covered at different temperatures, and also by the large temperature range studied. The nine mean values for the five temperatures recorded in Table IV were all plotted on one curve, and the activation energy calculated both from the slope of the line and by least squares. The value is $E = 11{,}400$. The value of $\log PZ$ is 3·91.

DISCUSSION.

The reaction is predominantly of the second order with respect to the sulphur trioxide. The constants themselves show a certain trend, which may be due to experimental error, since the manipulation of sulphur trioxide solutions is difficult, or it may be real. The latter possibility is suggested by the consistency with which the points lie on the curves in Fig. 2, each point referring to a separate filling of the reaction tube: the variations from one run to another may therefore be due to some uncontrolled factor, such as a certain indeterminateness in the state of the dissolved sulphur trioxide, rather than to mere manipulative errors. However this may be, there is little doubt that the predominant reaction is of the second order, and that therefore the mechanism involves either two molecules of SO_3 or a molecule of S_2O_6. The molecular complexity of solid sulphur trioxide is variable, but in these nitrobenzene solutions it must be predominantly monomeric. Otherwise, if it were dimeric and the monomer reacted, the rate would be proportional to the square root of the concentration, while if it were dimeric and the dimer reacted the rate would be proportional to the first power of the concentration. The approximately second order observed demands that two molecules of the species predominantly present should react: this is only likely to be satisfied with two molecules of the monomer. Whether these two molecules enter separately into reaction or as a pair in the form of a molecule of S_2O_6 cannot be decided definitely, but the following considerations are relevant as a guide to further investigation.

The second SO_3 may be involved in a specific interaction with the nitro-group, which influences the reactivity of the whole nucleus. This can be settled by finding the order of reaction with other aromatic substances.

On the other hand, there might be some mechanism whereby the second SO_3 facilitates the transfer of the replaced proton from carbon to sulphur, in a manner formally analogous to that in which a basic catalyst acts in other reactions.

Finally, there is the possibility that the molecule S_2O_6, about which little is known, may have a charge distribution which makes it a more powerfully kationoid reagent than SO_3 itself. In this connection it is of interest to note that Michael and Weiner (*J. Amer. Chem. Soc.*, 1936, **58**, 294), on the evidence of certain preparative reactions, do in fact consider S_2O_6 to be the active agent in sulphonations.

Until further evidence on these questions is obtained, detailed analysis of the statistics of the reaction must be deferred, but the following comparison is of interest. The activation energy is 11,400 cals. and log PZ is 3·91. In the reaction of esterification where two molecules of acetic acid react with the polar solvent ethyl alcohol, the value of this term is 3·69. If, therefore, the sulphonation reaction be regarded as one of two molecules of SO_3 with the polar solvent nitrobenzene, then we see that the reaction probabilities, *i.e.*, of correct orientation and energy redistribution, would appear to be of the same order as in the esterification reaction, where, in fact, the reaction probability, or entropy of the transition state, is small.

TABLE I.

Sulphuric acid present initially and finally, showing absence of appreciable sulphone formation.

(1) = Initial titre in c.c. of N/20-alkali. (2) = Initial titre − 2 × titre drop on reaction. (3) = C.c. of N/20 equivalent to the weight of barium sulphate from the end-product.

(1).	(2).	(3).	(1).	(2).	(3).	(1).	(2).	(3).
245·0	149·1	142·6	112·8	8·7	3·4	66·5	5·6	8·9
206·4	119·6	116·2	95·5	13·2	9·4	50·1	14·8	13·1
193·5	6·4	8·8	77·1	15·1	11·1	44·8	7·5	7·9
169·3	9·1	9·7	74·7	3·3	6·8	34·3	8·6	9·5
134·9	7·0	10·0	74·2	21·6	20·1	31·1	12·7	12·6
136·1	10·4	3·5	71·0	10·8	8·8	28·9	8·1	8·0

TABLE II.

Initial rates of reaction. Temp. 40°.

Initial SO_3, g.-mol./l.	0·893	0·612	0·557	0·516	0·484	0·331	0·308	0·278
Initial rate, per cent./min.	0·59	0·35	0·31	0·29	0·24	0·16	0·14	0·14

TABLE III.

Data for typical series of experiments at 60°. *Initial* SO_3 *concentration* = 0·974 *g.-mol./l.*

(a)

x, %.	$\Delta x/\Delta t$, %/min.	$\sqrt{\frac{1}{(a-x)^2}\frac{\Delta x}{\Delta t}} \times 10^3$.	x, %.	$\Delta x/\Delta t$, %/min.	$\sqrt{\frac{1}{(a-x)^2}\frac{\Delta x}{\Delta t}} \times 10^3$.
10·0	1·400	13·2	50·0	0·039	3·94
16·8	0·918	11·5	54·0	0·029	3·67
20·0	0·785	11·1	59·8	0·020	3·51
28·4	0·516	10·0	64·0	0·0054	2·03
30·0	0·467	9·76	69·3	0·0044	2·18
38·4	0·199	7·25	73·2	0·0021	1·72
40·0	0·169	6·86	77·8	0·0013	1·63
46·9	0·063	4·72			

(b) Values of a: experimental, and calculated from K = 13·5 (K is expressed with concentrations in g.-mols./l.).

x, %	10	20	30	40	50	60	70	80	90
a, exptl.	0·895	0·777	0·635	0·459	0·280	0·186	0·135	0·107	0·088
a, calc.	0·899	0·777	0·634	0·474	0·322	0·211	0·147	0·110	0·087

(c) Values of k [k expressed in (l./g.-mol.)/sec.].

x	15	20	25	30	35	40	45	50	60	70
$\Delta x/\Delta t$ ...	1·030	0·785	0·602	0·467	0·315	0·169	0·0775	0·039	0·020	0·0040
a	0·845	0·777	0·710	0·634	0·555	0·474	0·395	0·322	0·211	0·147
$k \times 10^4$...	3·42	3·48	3·66	4·06	4·14	3·58	2·80	2·58	4·82	3·52

TABLE IV.

Values of k.

	Temp. 80°.			Temp. 60°.	
Initial SO_3.	Mean 10^4k from $k = (\Delta x/\Delta t)/a^2(a - x)^2$.	10^4k from initial rate.	Initial SO_3.	Mean 10^4k from $k = (\Delta x/\Delta t)/a^2(a - x)^2$.	10^4k from initial rate.
0·883	6·72	6·72	0·974	3·61	3·78
0·735	7·48	5·96	0·893	2·96	2·48
0·625	6·68	8·28	0·629	2·62	1·72
0·556	4·72	7·48	0·411	2·34	2·90
0·520	5·72	6·00	0·286	1·98	2·16
0·371	2·72	3·70			
0·309	3·44	2·90	0·554 *	3·40	—
0·301	4·98	5·96	0·154 *	2·94	—
0·170	3·82	4·02			
0·078	4·44	5·44			

* Product added initially—see Table V.

Mean values for various temperatures, (l./g.-mol.)/sec.

Temp.	100·4°	80·0°	60·0°	40·0°	25·0°
10^4k_{formula}	16·3	5·07	2·81	0·79	—
$10^4k_{\text{initial rate}}$	16·8	5·56	2·61	0·90	0·33

TABLE V.

Addition of product. Temp. 60·0°.

Initial SO_3.	Initial H_2SO_4.	Initial sulphonic acid.	$k \times 10^4$.
0·154	0·037	0·148	2·94
0·554	0·055	0·145	3·40

(In the first experiment the initial rate was about one-sixth and in the second about one-half of that in the absence of product.)

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