

reaction, and the mere isolation of that lactone on evaporation of the chloroform. Similar considerations apply when the oxidation is conducted in the presence of an excess of calcium carbonate, with the additional complication that under these conditions most of the product may pass through the stage of the calcium salt from which the organic acid, not the lactone, is liberated on acidification. The experimental procedure of these authors is ill-adapted to the problem they have in view and definite conclusions concerning the preferential formation of either lactone during the oxidation cannot be drawn from their present results.

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RECEIVED APRIL 13, 1932
PUBLISHED JUNE 6, 1932

THE EFFECT OF FOREIGN GASES ON UNIMOLECULAR REACTIONS

Sir:

The recent communication by Steacie [THIS JOURNAL, 54, 1695 (1932)] suggests a generalization that has apparently not been made hitherto, *viz.*, that foreign gases do not activate unimolecular reactions. The earliest experimental evidence on this subject is the work of Daniels [THIS JOURNAL, 47, 1602 (1925)], who showed that the rate of decomposition of nitrogen pentoxide in the presence of nitrogen falls off at about 0.01 mm. partial pressure. Later experiments show that the behavior is the same in the absence of nitrogen.

The conspicuous exception to this generalization is the action of hydrogen on certain organic compounds at elevated temperatures. The explanation of this exceptional behavior is to be sought in the fact that a reaction between the hydrogen and organic molecule would be predicted by an organic chemist.

While we do not know much about the conditions under which translational energy is converted into vibrational energy [see Kassel, Rice, *Chem. Rev.*, 10, 11 (1932)], the evidence is that this process does not take place readily. The early attempts to calculate the limiting pressure for the unimolecular decomposition of nitrogen pentoxide were without significance because only translational energy was considered.

On the other hand, vibrational energy is only transferred readily when there is a sharp resonance between the colliding molecules.

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RECEIVED APRIL 25, 1932
PUBLISHED JUNE 6, 1932