

FIG. 6. The ratio of steady-state concentrations of  $C_4D_3$  and  $C_4D_2$  at about 2000°K plotted against the initial concentration of acetylene. Triangles: 7½%  $C_2D_2$  and neon; open circles: 5%  $C_2D_2$  and neon; half-solid circles: 17%  $C_2D_2$  and neon; squares: 5%  $C_2H_2$  and neon.

When the radical  $C_4H_3$  reaches a steady-state concentration, this mechanism gives the rate of formation of diacetylene

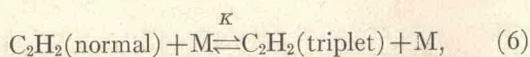
$$d[C_4H_2]/dt = k_3[C_4H_3][M] = k_1[C_2H_2]^2 \quad (h)$$

If the rate of formation of diacetylene by Eq. (h) is identified with the rate of pyrolysis of acetylene [Eq. (c)], the earlier presented calculation of  $k_2$  is justified. At a later stage in the reaction when both  $C_4H_3$  and  $C_4H_2$  reach steady-state concentrations, the mechanism embodying Reactions (1) to (5) leads to the expression:

$$\text{in steady state: } [C_4H_3]/[C_4H_2] = (k_4/k_3)[C_2H_2], \quad (i)$$

which is in agreement with experimental data shown in Fig. 6.

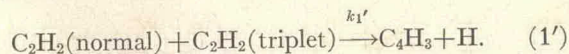
The mechanism, however, aside from not providing for the elimination of hydrogen atoms, presents other serious difficulties. The activation energy of the pyrolytic reaction [Eq. (c)] is in very satisfactory agreement with the heat of Reaction (1) since the reverse reaction should have only a very low activation energy. However, the pre-exponential factor in Eq. (c) is about as large as the collisional frequency, while a steric factor of  $10^{-3}$  would be more reasonable.<sup>27</sup> This may not be a decisive difficulty if, following others,<sup>28</sup> we assume that an "equilibrium" is established:



<sup>27</sup> S. W. Benson, *Foundations of Chemical Kinetics* (McGraw-Hill Book Company, Inc., New York, 1960), p. 280.

<sup>28</sup> See, for example, Ref. 9.

where  $K$  is the equilibrium constant, and Reaction (1) is instead



Then  $k_1 = k_1'K$  and the larger entropy of the triplet state, if it is not linear,<sup>29</sup> would result in the pre-exponential factor of  $k_1$  being larger than normal.

The triplet state of acetylene is very reactive<sup>30</sup> but for this mechanism to be acceptable the energy of the triplet state must be no higher than 42 kcal<sup>29</sup> and the singlet  $\rightleftharpoons$  triplet transition must occur very readily on collisions for the equilibrium to be established rapidly enough. If Reaction (3) has an activation energy of no more than 50 kcal, it can be estimated to be fast enough to account for the observed rate of the establishment of steady state in  $C_4H_3$ . However, the sum  $\Delta H_1 + \Delta H_3 = 106$  kcal is known reasonably accurately<sup>22</sup> and since  $\Delta H_1$  cannot be much larger than 42 kcal, 50 kcal for  $\Delta H_3$  is definitely too low. Furthermore the calculated  $\Delta H_4$  is much too positive to reconcile with the observed rapid increase in the steady-state concentration of diacetylene with temperature. Finally, the mechanism does not dispose of hydrogen atoms. The reaction  $C_2H_2 + H \rightarrow C_2H + H_2$  could be fast enough<sup>23</sup> only if its activation energy is less than about 15 kcal. The mass peak of this radical is unfortunately obscured by that of a fragment ion from acetylene and could not be identified. Further discussion of this and other reactions of hydrogen atoms and free radicals involved would be a pure speculation and seems not justified on the basis of limited experimental data available. However, we wonder whether the mechanism of isotopic exchange between acetylene and deuterium proposed by Kuratani and Bauer<sup>31</sup> is the correct one. In view of our data it could involve the primary formation of hydrogen atoms by Reaction (1), their isotopic exchange with deuterium molecules, and then Reaction (2). However such explanation calls for a different rate law from that reported by Kuratani and Bauer, and we are not able to resolve this difficulty. A free-radical mechanism of the thermal decomposition of acetylene and the nature of the primary reaction we believe, however, to have been established rather firmly.

#### ACKNOWLEDGMENT

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<sup>29</sup> C. K. Ingold and G. W. King, *J. Chem. Soc.* **1953**, 2702.

<sup>30</sup> C. A. Arrington and G. B. Kistiakowsky (to be published).

<sup>31</sup> K. Kuratani and S. H. Bauer, *J. Am. Chem. Soc.* **87**, 150 (1965).