

CHANGE IN THE HYPERFINE STATE OF THE HYDROGEN ATOM DURING ITS COLLISIONS
WITH UNSATURATED HYDROCARBON MOLECULES IN THE GASEOUS STATE

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The method put forward in^[1] is used to investigate collisions between hydrogen atoms and unsaturated hydrocarbon molecules by studying the attendant change in the hyperfine state of the hydrogen atom. A hydrogen maser operating on the $\Delta m_F = 0$ ground-state transition of the hydrogen atom was used as a highly sensitive spin relaxometer. The rate constant for the process is related to the characteristic time of the relaxation process induced by it through the formula $T_{1,2}^{-1} = K_{1,2} n_M$, where n_M is the density of the molecules under consideration in the maser chamber. All processes other than those under investigation were eliminated by using low reagent densities. The rate constants for the change in the hyperfine state of the hydrogen atom during its interaction with butene-1 and transbutene-2 have been measured and in addition the temperature dependence of the constant was determined for ethylene, deuterio-ethylene, propylene, isobutylene, cis-butene-2, and acetylene. The values obtained are in agreement with chemical reaction parameters available in the literature (to within the experimental error), i.e., $K_1 = K_2 \approx K_{\text{chem}}$. This result has been used to deduce a number of conclusions on the nature of the chemical reactions occurring in the systems under investigation.

THE elucidation of the nature of elementary chemical processes requires a knowledge of the interaction in the rarefied gaseous phase between atoms and molecules capable of entering into chemical reactions. In the present work we used a method proposed elsewhere^[1] to investigate collisions between hydrogen atoms and unsaturated hydrocarbon molecules by studying the change in the hyperfine state of the hydrogen atom.

A hydrogen maser, using the hyperfine transition ($F = 1, m_F = 0$) \rightarrow ($F = 0, m_F = 0$) in the hydrogen atom, was employed as a high-sensitivity spin relaxometer. When the density of hydrogen atoms in the upper maser state was well below the threshold value for generation in the maser chamber, the initial amplitude of the signal radiated at $\lambda = 21$ cm ($f = 1420.405$ MHz) which was excited by a short 90° pulse of the resonance frequency was proportional to the relaxation time T_1 of the population difference between the working levels, while the time constant of the exponential decay of the signal was equal to the relaxation time T_2 of the oscillating magnetic polarization of the hydrogen atoms.^[2,3] The time T_1 was measured by the method described in^[1] by looking at the initial amplitude of the signal as a function of the time interval between the instants at which the supply of atoms to the vessel was stopped and the 90° pulse was applied to the resonator.

EXPERIMENTAL METHOD

A block diagram of the apparatus is shown in Fig. 1. The inversion of the working levels is produced by passing the hydrogen atomic beam through an inhomogeneous magnetic field. Atoms in the $|1, 0\rangle$ state and those in the $|1, 1\rangle$ state are introduced through a capillary tube into the storage vessel placed in a microwave resonator maintained at a constant temperature by a

thermostat. The chamber walls are suitably coated to ensure that the hydrogen atoms remain there without change in the spin state for periods of 0.3–0.4 sec. The working density of the hydrogen atoms was 10^7 – 10^8 atom/cm³. The gases were leaked directly into the storage chamber from a gas-handling system through a diaphragm punched in a thin foil. The steady-state gas density in the chamber was measured to within 3% by determining the density in the reservoir, the rate of loss of gas from the reservoir, the volume of the reservoir, and the transmission of the capillary. The design of the system is described in detail in^[4].

The 90° pulse was produced by a highly stable quartz oscillator and was introduced through the resonator coupling loop. The maser radiation was picked-off by a second loop. A broad-band electron-beam parametric amplifier with a noise factor of 1.4 and 25 dB amplification was used as a preamplifier. The receiver was a superheterodyne with triple frequency transformation and the following output parameters: frequency 5.7 kHz and bandwidth 150 Hz. The sensitivity of the receiver was 2×10^{-18} W.

The amplified signal was detected and then fed into a recording system. The parameters of the detected maser signal, which was of the form $A \exp(-t/T_2)$, were determined from the values of the signal integrals I_1 and I_2 after successive equal intervals of time t_1 :

$$T_2 = t_1 / \ln \frac{I_1}{I_2}, \quad A = \frac{I_1^2}{(I_1 - I_2)t_1} \ln \frac{I_1}{I_2}.$$

The integrator was based on an amplitude-frequency converter and two adding circuits, Σ_1 and Σ_2 . The characteristic times in the range 20 μ sec to 1 sec were determined to better than 1% and, moreover, the use of the integration principle resulted in a substantial reduction in the receiver noise.

Gas	$K_1 \cdot 10^{12}$, cm ³ /sec						K_1/K_2	$K_2 = K_2^0 \exp(-E_{act}/RT)$	
	11° C	17° C	19° C	27° C	37° C	47° C		E_{act} kcal/mole	$K_2^0 \cdot 10^{12}$, cm ³ /sec
C ₂ H ₄	0.840		1.00	1.09	1.20	1.29	0.98 ± 0.03	1.71 ± 0.05	1.89 ± 0.11
C ₂ D ₄	0.70		0.81	0.88	0.99	1.17		2.70 ± 0.09	7.83 ± 0.54
C ₂ H ₂	1.38		1.62	1.73	1.85	2.01	1.00 ± 0.02	1.48 ± 0.08	2.07 ± 0.10
i-C ₃ H ₈				3.46	3.66	3.42	0.97 ± 0.04	0.4 ± 0.2	0.44 ± 0.02
cis-C ₄ H ₈ -2		3.40		1.07	1.21	1.32	0.97 ± 0.03	1.97 ± 0.09	3.31 ± 0.15
Trans-C ₄ H ₈ -2		0.96			0.10				
i-H ₂ -1			0.246	1.80					
i-H ₂				0.299	0.384	0.439	1.04 ± 0.05	4.14 ± 0.30	30.0 ± 1.0

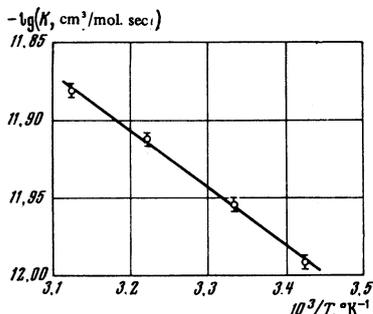


FIG. 2. Rate constant for $H + C_2H_4$ as a function of temperature.

crepancies are usually no greater than 5–10%. The relative rate constants averaged over the results reported in^[6-10] are given below:

Gas:	C ₂ H ₄	C ₂ D ₄	C ₂ H ₂	i-C ₃ H ₈	1-C ₃ H ₈	C ₄ H ₈ -2
Published data:	1	1.00	1.60	4.00	1.63	0.96
Our data:	1	1.03	1.60	3.60	1.60	0.96

The absolute rate constants at room temperature were measured reliably only for the reaction $H + C_2H_4 \rightarrow C_2H_3^*$. The agreement between the data reported by different workers is much worse in this case. The most reliable results are those reported in^[10-14] and lie in the range $1.0 \pm 0.4 \times 10^{-12}$ cm³/sec.

The temperature dependences of the rate constants have been measured reliably also for the reaction $H + C_2H_4$. Assuming that the Arrhenius law describing the change in the rate constant with temperature was valid ($K = K_0 e^{-E/RT}$), it was found that the effective activation energy E was as follows (kcal/mole): 2.0 ± 0.8 ,^[15] 1.64 ± 0.36 and 1.77 ± 0.45 .^[16] For acetylene, kinetic measurements have been carried out only at a pressure of a few torr.^[17] The rate constants for the attachment of the hydrogen atom cannot be calculated from these values because of the short lifetime of the resulting free radical $C_2H_3^*$.

The rate constants for the change in the hyperfine structure of the hydrogen atom during interaction with a molecule M and for the loss of coherence by the atom during this interaction (K_1 and K_2 , respectively) are, of course, only the upper limits for the rate constant for the chemical reaction between the partners, since the reaction is definitely known to lead to these processes. Let us consider the interaction between the partners in greater detail.

When the hydrogen atom collides with a molecule with paired electrons, the probability of a change in its hyperfine structure during the collision time is very small. This is indicated both by theoretical estimates and by the experimental data obtained by Berg.^[18] It follows from his data that the corresponding cross sections for the N_2O , CO , and CO_2 molecules do not exceed

10^{-18} cm², whereas for Xe the number is 10^{-20} cm². The situation is drastically modified when the interaction is accompanied by a substantial change in the electron configuration of the molecule, i.e., there is partial or complete unpairing of its valence electrons. In this case, we have a spin exchange or dipole-dipole interaction between the electrons in the hydrogen atom and in the molecule, and an increase in the interaction time due to the formation of the compound quasimolecule which leads to a considerable increase in the probability of a change in the spin state of the hydrogen atom. Since the distance between the partners is then quite small, this probability is probably close to unity. One may therefore suppose that the rate constant measured by the present method corresponds to the unpairing of the valence electrons in the molecule during its collision with a hydrogen atom.

Comparison of our measurements of the rate constants for the change in the spin state of the hydrogen atom, K_1 and K_2 , with the rate constant K_{chem} for the corresponding chemical reactions shows that all the measured quantities agree with the chemical reaction parameters published in the literature (to within the experimental error in the latter), i.e., $K_1 = K_2 \approx K_{chem}$. This fact enables us to draw the following conclusions as to the nature of the chemical reactions in the above systems:

1. In all the cases we have considered, an appreciable change in the electron configuration of the molecule during its interaction with the hydrogen atom in the gaseous phase leads to reactions between the partners with probability close to unity.

2. The fact that $K_1 = K_2$ suggests that when collisions occur between hydrogen atoms and the above molecules there are no coherent (e.g., spin exchange) processes (if this were so, we would expect $K_1 > K_2$) or adiabatic processes connected with the violation of coherence (this would correspond to $K_1 < K_2$), and the probability for this is comparable with the probability for the chemical reaction.

3. The fact that both K_1 and K_2 are equal to K_{chem} is also an experimental confirmation of the assumption that the rate constant for the formation of the free radical, extrapolated to high pressures, is equal to the rate constant for the elementary event of attachment of a hydrogen atom to a multiple bond of a hydrocarbon. In its turn, this equality suggests that a) these processes are not accompanied by the appearance of excited particles with short ($\lesssim 10^{-9}$ sec) decay lifetimes, which cannot be stabilized by the pressure reached in the experiment on the determination of the rate of chemical reactions in the gaseous phase, b) the probability of disintegration of the excited radical during its collision with the molecule in the medium is much less than the

probability of deactivation as a result of this, and c) the probability of the formation of an excited free radical $C_nH_{k+1}^*$ from the initial quasimolecule, if such exists, is close to unity.

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