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MEASUREMENT OF CHEMICAL POLARIZATION OF THE NUCLEAR MAGNETIC MOMENT OF GASEOUS REACTION PRODUCTS

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NMR investigations of the kinetics of the nuclear moment of gaseous products released in the chemical reaction of the decomposition of an organic peroxide make it possible to observe the chemical polarization of protons of methane (dynamic gain coefficient $E = 1 \times 10^3$) and ethane ($E \approx (3-6) \times 10^2$). It is shown that the kinetics of the nuclear moment of chemically polarized nuclei of the gaseous product constitutes the kinetics of formation of the gaseous products with a chemical-polarization constant slowed down by diffusion, $M(t) \approx M_0 e^{-3at/5}$, where a is the reaction-rate constant.

IN[1,2] we proposed and realized experimental methods for determining the coefficient of dynamic amplification of nuclear polarization in a chemical reaction that proceeds in the liquid phase. The present paper is devoted to the development of analogous methods in the special case of gaseous products that are removed rapidly from the investigated volume during the course of the reaction.

1. CALCULATION OF THE NUCLEAR MOMENT AND ITS KINETICS

The observed intensity of the NMR signal from nuclei belonging to the investigated gas is proportional to the total magnetic moment of these nuclei M(t), and in the most general case

$$M(t) = \mu p_0 k(t) f(t), \qquad (1)$$

where μ is the magnetic moment of the nucleus, p_0 is the equilibrium polarization of the nuclei, k(t) is the time dependent effective gain of the nuclear polarization, f(t) is the number of gas molecules contained in the volume of the investigated sample. The coefficient k(t) depends on the time by virtue of the fact that the number of the newly produced molecules, the nuclei of which are chemically polarized, i.e., have a polarization Ep_0 (where $E \neq 1$ is the dynamic gain), changes as the initial substance becomes consumed, and the thermal relaxation tends continuously to establish the equilibrium value of the polarization p_0.

We consider the reaction $C \to \dot{R} \to F$ ($\dot{R}$—free radical), during the second stage of which there occurs chemical polarization. Let the rate of the reaction be determined by the rate of decomposition of the initial matter and let the production of the gas be determined by the expression

$$df^* / dt = af_0 e^{-at}, \qquad (2)$$

where f*(t) is the number of gas molecules released from the volume at the instant t (the reaction begins at t = 0); f_0 is the total number of gas molecules released at the end of the reaction; a is the reaction rate constant. Equations (1) and (2) are referred to unit volume, as is also f_0. If we consider the total magnetic moment of all the released gas molecules, M*(t), then we can write

$$dM^* / dt = E\mu p_0 af_0 e^{-at} - \alpha(M^*(t) - \mu p_0 f^*(t)),$$

where α is the rate of thermal relaxation. However, the experimentally observed magnetic moment belongs only to the molecules situated in the investigated volume, and therefore the kinetics of M(t) differs significantly from the kinetics of M*(t), and is determined by the gas-release processes. The investigated sample under conditions of gas release is a heterogeneous system (gas bubbles in a saturated solution). The produced gas bubbles have a radius r, which equals, if the surface tension of the solution is σ and the external pressure is P (we neglect the hydrostatic pressure of the solution),

$$r = 2\sigma / P \approx 10^{-2} \text{ cm}. \qquad (3)$$

The time required for the bubbles to float out of the working volume of the coil in the case of ordinary organic solvents at atmospheric pressure and at a temperature close to 100°C is approximately one second. It might seem that the observed NMR signal receives also a contribution from the molecules of the gas phase. However, in view of the rapid thermal relaxation in the gas phase (for methane, for example, the relaxation times T_{1n} in the gas and in the liquid differ by three orders of magnitude[4], and in a gas $T_{1n} < 0.1$ sec), the NMR signal from the gas phase cannot be observed. The chemical polarization should be retained only in molecules that are kept in the solution. The lifetime of the molecule in a supersaturated solution coincides with the time of bubble production. It can be assumed that the produced bubbles have identical dimensions. However, during the course of consumption of the initial substance, the volume in which the number of gas necessary for bubble production is released increases. The time during which the necessary amount of gas accumulates also increases, and the diffusion processes determine a certain delay between the time of gas release into the solution and formation of the bubble.

To estimate this delay time, we use the following considerations. The gas molecules released in a certain volume inside a sphere of radius R form a bubble with radius r < R (otherwise the solution would foam). The formation of this bubble occurs within a time τ_D equal to the time of diffusion and to a certain distance R, i.e., $\tau_D \approx R^2/2D$, where D is the coefficient of diffusion of the gas molecules in this solution. The number of gas molecules released during that time in a volume $4\pi R^3/3$ is equal to

$$n = f_0 a e^{-at} \frac{4\pi R^3}{3} \tau_D.$$

This number, on the other hand, is equal to

$$n = \frac{4\pi}{3} r^3 L,$$

where L is the number of gas molecules in a unit volume of the gas phase. From a comparison of the indicated relations we obtain for the gas-molecule concentration f(t) per unit volume of a sample in the form of a supersaturated solution and the lifetime τ_D of the gas molecules in the solution:

$$f(t) \approx (r/R)^3 L \approx 2^{-3/5} D^{-3/5} L^{2/5} f_0^{3/5} a^{3/5} r^{6/5} e^{-3/5 at} \tag{4}$$

$$\tau_D \approx 2^{-3/5} D^{-3/5} L^{2/5} f_0^{-2/5} a^{-2/5} r^{6/5} e^{-2/5 at}. \tag{5}$$

The rate of change of the average gas concentration in the investigated solution is equal, in the quasi-stationary approximation (in the time interval $(t - \tau_D/2) - (t + \tau_D/2)$)

$$f(t) / \tau_D \approx a f_0 e^{-at}, \tag{6}$$

i.e., it is equal to the rate of release of gas in the reaction in the same time interval. An estimate of τ_D at $D \approx 10^{-5}$ cm^2/sec, $L/f_0 \approx 10^{-1}-10^2$, $a \approx 10^{-2}-10^{-3}$ sec^{-1}, and $r \approx 0.5 \times 10^{-2}$ cm yields $\tau_D = 1-10$ sec. It follows from this estimate that, at least in the initial stage of the reaction, τ_D is much shorter than the time of thermal relaxation of the nuclear moment in the liquid. Therefore we assume in the expression for the observed summary nuclear moment (1) that the nuclear polarization is constant and is equal in magnitude to the chemical polarization of the newly produced molecules Ep_0.

A good control experiment for verifying the calculations presented above is the instantaneous destruction or inversion of the nuclear polarization when a radio-frequency pulse is applied (the method was proposed by us in[1,2]). In the case under consideration the restoration of the nuclear moment to the quasi-equilibrium value occurs via rapid forcing out of the depolarized nuclei by "fresh" chemically polarized ones. If the chemical polarization is much larger than the equilibrium value $|E| \gg 1$, the contribution to the NMR signal made by the normally polarized nuclei can be neglected, the rate of establishment of the quasi-equilibrium value g can be set equal to τ_D^{-1}, and the nuclear polarization can be regarded as constant even if $g \approx \alpha$. Measurements of M(t) and g(t) make it possible to study the reaction kinetics, since

$$M(t) \approx M_0 e^{-3at/5}, \tag{7}$$

$$g(t) \approx g_0 e^{-2at/5}. \tag{8}$$

The observed NMR signal is also determined usually by the characteristics of the apparatus, which are not known exactly. Therefore, to determine the dynamic gain in chemical polarization, E, it is necessary to determine independently f_0 and to calibrate the spectrometer against the NMR line intensity of a standard substance contained in a solution of known (absolute or relative) concentration.

Formulas (7) and (8) admit of generalization to the case when several different gaseous products are released in the course of the reaction, and M(t) belongs to one of them. If the kinetics under which all the gases are produced is determined by the rate of decay of the initial substance, and the difference between the diffusion coefficients can be neglected, then the result is perfectly analogous to (7):

$$M_i(t) = \mu p_0 \varepsilon_i(t) F(t) E, \tag{9}$$

where F(t) is the total concentration of the gases per unit volume, $\epsilon_i(t)$ is the partial concentration of the investigated gas, which coincides with (1) by virtue of the equality $f_i(t) = \epsilon_i(t) F(t)$.

In concluding this section, we present a fundamental working formula that follows from (6) and is suitable for the calculation of the gain E:

$$E_i = \frac{I_i(t)}{I_e(t)} \frac{m_e k_e(t)}{m_i} \frac{n_e}{n_i} \frac{1}{\tau_D a} e^{at}, \tag{10}$$

where $I_i(t)$ and $I_e(t)$ are the intensities of the NMR signals of the investigated and standard lines, respectively, at the instant of time t; n_i and n_e are the numbers of the nuclei in the molecules of the investigated and standard substances; k(t) is the effective gain of the magnetic moment of the standard substance; m_i and m_e are the molar yields of the investigated and standard substances in the reaction. We start from the fact that a convenient standard may be the chemically polarized nuclear moment of the known product accumulated during the process of the reaction (the kinetics of such a magnetic moment was considered by us in[1,2]), inasmuch as the extraneous impurities participate actively enter in side reactions, or influence the course of the main reactions.

2. EXPERIMENT

We investigated the kinetics of the nuclear magnetic moment of methane CH_4, which is released during the course of thermal decay of organic peroxide $R_1COOOCOR_2$, where R_1 or $R_2 = CH_3$, in organic solvents (solutions 0.2–0.8 N) at temperatures 90–120°C. The spectra of the proton magnetic resonance were taken, using the procedure described in[1], at 60 MHz with the Varian DA-60-IL instrument. During the first 50–70 seconds, the sample was heated to the temperature at which the reaction was investigated (the growth of the signal was not investigated in this stage).

1. General Character of the Kinetics of the Nuclear Moment

The experiments show (see Figs. 1–3) that, with the exception of the initial stage of the reaction, when heating and occasional foaming of the sample takes place, leading to irregularity in the reproduction of the NMR signals and in the dependence of the NMR signal (and consequently of the signal of the magnetic moment of the methane protons) on the time is well described by the exponential function

$$M(t) = M_0 e^{-k_1 t}.$$

Comparison with other independent measurements of the reaction rate constant yields, in accordance with the results of our calculation

$$k_1 \approx {}^3/_5 a.$$

This result confirms that chemical polarization of

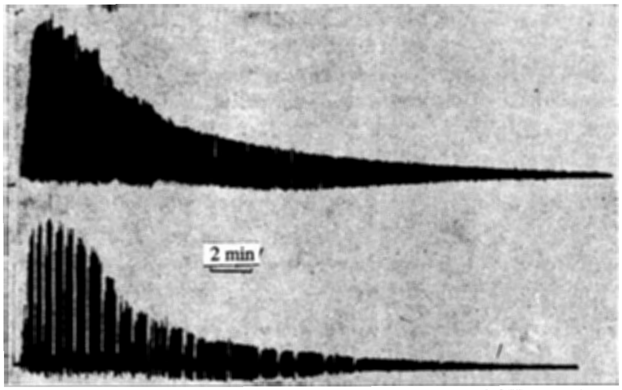

FIG. 1. Kinetics of the nuclear magnetic moment of CH_4 produced in the decay of the peroxide of acetylbenzoyl in C_2Cl_4 (112°C). a–Ordinary record, b–record with periodic destruction of the polarization by means of radiofrequency pulses.

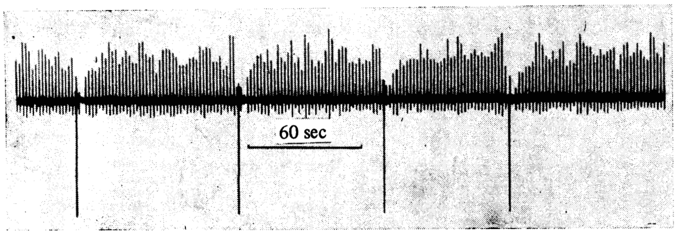

FIG. 2. Reconstruction of the nuclear moment of CH_4 after destruction of polarization by means of a short radiofrequency pulse (acetylbenzoyl in C_2Cl_4 at 90°C).

methane (it has a positive sign) is much larger than the equilibrium polarization and is constant during the process of the reaction.

2. Measurements of the Rate of Release of Methane from the Solution

We performed the experiment proposed in the preceding section, wherein nuclear polarization was destroyed by application of a radiofrequency pulse (in practice, by turning on a large radio frequency power for a short time). Further, the establishment of the quasiequilibrium value of $M(t)$ was investigated by rapid multiple registration of the NMR signal (see Figs. 1 and 3). The dependence of $M'(t)$ during the course of approach to the quasiequilibrium value is roughly approximated by the exponential function (Fig. 2) $M'(t) = M(t)(1 - e^{-gt})$ (deviations due to irregularities in the reproduction of the NMR signal reach 30% and sometimes more). In turn, the approximate values of $g(t)$ depend on the time approximately exponentially

$$g(t) \approx g_0 e^{-k_2 t},\ k_2 \approx {}^2/_5 a.$$

In order of magnitude, the time of re-establishment of the nuclear polarization, as expected (see the preceding section), lies in the range 3–20 sec.

The calculated (see (5)) and the observed values of τ_D are in good agreement. We note that if we take into account the release of methane only we obtain $\tau_D \approx 30$ sec at 110°C for a solution of acetylbenzoyl peroxide. Bearing in mind, however, the fact that the main gaseous product is CO_2, we obtain at the same stage of the reaction $\tau_D \approx 5$ sec. Thus, these additional experiments give an independent, albeit rough but evident confirmation of the calculations of the preceding section. It can be assumed that the chemical polarization of the methane is large and the kinetics of its nuclear moment is determined by the diffusion and the change of the exchange of the gas in the solution, and not by thermal nuclear relaxation. Our observations show that the kinetics of the nuclear magnetic moment of chemically polarized gaseous products serves as a unique method for determining the kinetics of the reaction and for investigating the processes of the release of the gas from the solution. The total amount of the gas released per unit volume can be estimated, in accordance with (5) from the measured value of τ_D, if one knows the surface tension of the solution and the pressure (i.e., the radius of the bubble) and the reaction rate constant.

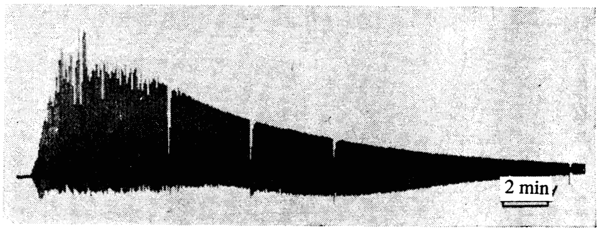

FIG. 3. Kinetics of nuclear magnetic moment of CH_4 in the decay of 0.36N of the solution of peroxide of acetylbenzoyl in C_2Cl_4 at 106°C. During the initial stage of the reaction, foaming takes place.

3. Measurements of the Coefficient of Dynamic Amplification in the Formation of CH_4

The final purpose of the present work was to measure the dynamic gain E. To this end we used formula (10). An advantage of the formula proposed by us is that all the quantities that enter in it can be measured by using the NMR method directly in the ampoule of the spectrometer, and its use does not make it necessary to employ data obtained under other conditions (yet many details connected with the change of the investigated volume, the temperature conditions, etc., can noticeably influence the course of the reaction). The values of the relative molar yields of the different products in the decay of the peroxide of acetylbenzoyl ($R_1 = CH_3$, $R_2 = C_6H_5$) were estimated by integrating the NMR signal after the end of the reaction. By estimating by the same token the yield of the products remaining in the solution and containing CO_2 and CH_3, it is possible to calculate the yield of the gaseous products CO_2 and CH_4, on the basis of the known chemical data[5] (also confirmed by our experiments) concerning the relative stability to the action of C_6H_5 group radicals and of benzene. The standard signal was the negatively-polarized proton line of the OCH_3 group of methylbenzoate $CH_3OCOC_6H_3$, the kinetics of which was investigated by us earlier[1], and also offers evidence of the comparative stability of these protons during the process of the reaction. The relative molar yields of methane and methylbenzoate turned out to be approximately equal (0.22 mole per mole of peroxide) also in the decay of 0.36 N of the solution in C_2Cl_4 at 110°C. The signals of OCH_3 of methylbenzoate and CH_4 turned out to be approximately equal in absolute magnitude at the instant of time t corresponding to the equality

$$e^{-at} \approx 0.25,$$

with $a \approx 1/270\ \mathrm{sec}^{-1}$ and $k_e(t) \approx -12$. At this stage of the reaction, the measurements yield $\tau_D \approx 10$ sec. With accuracy reaching ±30% according to our estimates, we obtain $E = 1 \times 10^3$ from (10).

In order of magnitude, the chemical polarization is the same in the entire investigated temperature and concentration range, and also in the decay of a number of other peroxides. We notice that methane is produced in the reaction $CH_3 + HX = CH_4 + \dot{X}$, and thus, the measured polarization is an average of the polarization of the protons of CH_3 and of the joined proton.

4. Estimate of the Gain of Chemical Polarization in the Formation of Methane

Without having more accurate data on the yield of ethane C_2H_6 in the same reaction (but in the presence of iodine I_2) (it is difficult to establish the yield of the ethane by NMR methods), we nevertheless can estimate the order of magnitude of the C_2H_6 polarization, starting from data on the gas analysis and from a comparison of the intensity of the CH_4 and C_2H_6 signals. Under the indicated conditions the yield of the ethane amounts to about 50% of the yield of the methane (according to our gas-analysis data), the NMR signal of the ethane is negatively polarized, and its absolute magnitude is about one-third that of methane. The use of formula (10) permits an estimate of the gain in the ethane (assuming that E for the methane is the same as in the absence of iodine). In order of magnitude, $E \approx (3-6) \times 10^2$ (the uncertainty of the estimate is connected with the fact that the time τ_D was not measured directly in this experiment.

5. General Remarks

We have succeeded, by observing the kinetics of nuclear magnetic moments of chemically polarized gaseous products, to find new possibilities in the investigation of both the chemical polarization and the kinetics of the reaction. The method of radiofrequency destruction of polarization has made it possible to employ nuclear magnetic resonance for the investigation of the processes in which gas is released from a solution and to confirm the simplest physical notions concerning the character of these processes.

The observed causes of the coefficients of dynamic amplification of the nuclear polarization in the formation of methane and ethane agree with the general concepts developed by us earlier[1]. The indicated quantities do not agree with the model of polarization in the free radical, at thermal equilibrium of all the degrees of freedom with the exception of the spin ones, and presuppose dynamic polarization in the activated paramagnetic complex under conditions when the thermal equilibrium with the lattice is violated (i.e., arbitrarily speaking, polarization in the act of the chemical reaction).

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